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EFFECT OF APPLIED STRESS, THERMAL ENVIRONMENT AND WATER IN EPOX--ETC(U)

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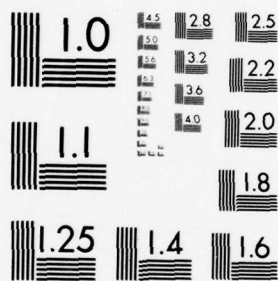
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EFFECT OF APPLIED STRESS, THERMAL
ENVIRONMENT AND WATER IN EPOXY RESINS

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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) The DGEBA/TETA system was examined in postcuring conditions at 100degree C of three and six days. Sorption kinetics and equilibria at different temperature and mechanical tests have been performed on the two sets of samples. Attention was also given to the effects on solubilities of thermal history in presence of water. It was observed that the saturation values in such systems are determined once the higher temperature of the thermal cycle is defined. The differences in solubilities of samples with different hygrothermal history are explained in terms of microcavities that can be formed by effect of crazing in the plasticized			

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system exposed to high temperatures. Solubility in the resins was then found to be a decreasing function of temperature while void volume percent an increasing function of the same. Mechanical tests varified this hypothesis. ↗

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INTRODUCTION

Since composite materials, with polymeric matrices, are emerging as candidates for primary structures in aeroplanes it becomes very important to investigate their performance under various environmental conditions.

One of the most important problems is connected with the sorption and diffusion of water in the polymeric matrix thereby lowering the glass transition temperature of the resin and consequently altering the mechanical performance of the overall composite.

In this work a description of the penetrant diffusion and the effect of sorption on the physical properties of the polymer, as function of environmental conditions and thermal histories, has been attempted. Moreover, the interaction between water transport and various types of applied stresses will be the principal form of the future research program.

Literature results on water sorption in epoxy resins (1 -4) show that both the kinetics and the apparent equilibrium of the sorption phenomena can be strongly influenced by the history of temperature and humidity that the sample has undergone prior to the experiment. Arbitrary thermal spikes on saturated samples show (1,4)

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a dramatic effect on water solubility equilibrium values.

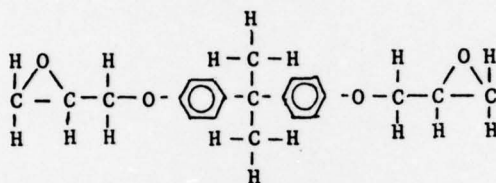
Although equilibrium cannot depend on the past history, polymeric systems may exhibit apparent equilibrium on a time scale so slow as to be inaccessible to experiment. These effects have been discussed in some detail (5, 6, 7).

In this work, we have performed a series of systematic experiments on water sorption in epoxy resins related primarily to the effects of postcure condition on the properties of the resulting cross-linked resins. The essential features of a well defined hygrothermal history on the apparent water sorption equilibrium is also considered.

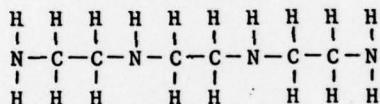
The results have been interpreted on the basis of a physical model, for which independent, albeit indirect, experimental support has been obtained.

EXPERIMENTAL

Specimens were prepared from Epikote 828 (Shell Co) using triethylene tetramine as curing agent (TETA Montedison Spa.).



Diglycidyl ether of bisphenol A (DGEBA)



Triethylene tetramine (TETA)

Distilled water was used in liquid and vapor sorption experiments.

Sample preparation

The resin and the cross-linking agent were hand mixed at room temperature in a 100 to 14 ratio without further purification and then vigorously mixed under vacuum for 15 minutes. The mixture was then poured in PMMA moulds of 0.6 to 3.0 mm in thickness, kept under

vacuum for 1 hr to completely degase the system and then kept in a dry atmosphere at 23°C for 24 hr.

Gel formation was usually acheived in about 1 hr. PMMA moulds were placed in a vacuum oven set a 80°C for 24 hr. The uncured resins were in fact brittle and it was very difficult avoid their breackage opening the moulds while after such a treatement epoxy resin specimens were easely detached. Specimens were finally cured at 100°C for three days. A second batch of sample was prepared identically, however the final curing period was increased to 6 days.

Samples were stored in a dessicator containing anydrous CaCl_2 .

Mechanical procedures

Clash-Berg experiments: mechanical test were performed by using a Clash-Berg torsional stiffness apparatus. Untrated 3 and 6 days cured samples, 60 mm x 10 mm x about 3.0 mm, otherwise identical samples previously immersed and saturated in water at 3 temperatures (23°, 45°, and 75°C) and saturated-dried samples were tested over a broad range of temperatures while the specimen was immersed completely in paraffin oil.

The angular deflection α was measured after application of a torque, M_t , for 10 seconds. The values of the shear moduli were calculated according with the following equation:

$$G(10) = 917 M_t l / u \alpha a b,$$

were a, b and l are, respectively, the width, thickness and length of the specimen and u is a tabulated parameter which depends upon the ratio a/b (8).

Stress-strain experiments: specimens were loaded in tension using a Instron tester equipped with a temperature controlled chamber for dry tests and with a thermostatted water bath for tests on saturated samples. Dumbell specimens of 5.0 cm x 1 cm x about 0.05 cm were used. Saturation was determined by following sorption experiments on identical thickness samples.

Several temperature for dry and saturated samples have been tested. Constant strain rate of about 1.0×1.0^{-1} min was used.

Sorption kinetics and equilibria

Gravimetric liquid sorption experiments were performed by weighing 3.0 cm x 3.0 cm x about 0.05 cm samples repeatedly on a Galileo Sartorius analytical balance following repeated immersion in water maintained

at constant temperature. The samples were removed from the bath, blotted, placed in a pretared weighing bottle, weighed and then replaced in the constant temperature water bath.

Vapor sorption kinetics and equilibria were determined using a Mc Bain (9) quartz helical spring microbalance serviced by a standard vacuum system. The quartz helical springs with a 0.5 to 5.0 mg/mm sensitivity were obtained from the Rocky Mountain Quartz Products, Cleveland (Ohio). The samples were maintained at constant temperature by circulating thermostatted water through a water jacket surrounding the sorption cell.

Water sorption values were indicated as S, percentage of weight gain on the dry weight, and plotted as a function of $\sqrt{t/l}$, where l is the thickness of samples ranging from 0.4 to 0.6 mm for thin specimens and from 2.0 to 3.0 mm for thick specimens, consistent with a Fickian sorption behaviour.

Sorption equilibria were achieved in a range of 2 to 8 weeks and 2 to 12 months depending on the temperature of the test respectively for thin and thick specimens.

RESULTS AND DISCUSSION

Effects of curing time lenght on mechanical properties and glass transition temperatures

Mechanical results in torsion experiments for the two batches of samples are reported in fig. 1. No significant differences for 3 and 6 days cured samples are evident either for shear modulus than for glass transition temperature.

Glass transition temperature was calculated as:

$$T_g = T_i + T_f / 2$$

where T_i and T_f are defined in fig. 1; it was found to be 135°C.

Effects of curing time lengt on sorption behaviour

Water sorption data for samples post-cured 3 are reported in fig. 2 and in fig. 3 for thin and thick specimens respectively. The four curves of fig. 2 refer to sorption into samples immersed in liquid water at four temperatures: 23°, 45°, 75° and 90°C, while in fig. 3 are referred only to 23°, 45° and 75°C. After

the saturation thick specimens were used in Clash and Berg experiments. Some of the thin samples, first preswollen in water at 90°C for two weeks, were dried under vacuum at temperature above glass transition for 24 hr and then weighed again in the dry state. The weight after such a treatment was systematically below the original weight, by an amount of about 0.4 -0.5%. This suggests that desorption of some molecular weight component (which may be either the cross-linking agent or monomer) may take place in the swollen state during the sorption test as observed in previous experiments by Faulkner and Coworkers (10) for trapped solvent in glassy systems (10, 11).

The formation of a polymer network may be in fact accompanied by a rise in the glass transition temperature of the system. The curing of an epoxy resin is an example of a cross-linking reaction in which glass transition temperature (135°C in our case) of the reacting system becomes higher than the reaction (curing) temperature (100°C in our case). The curing practically ceases, owing to diffusion control before all functional groups have reacted (12, 13, 14). In such a case in fact the reacting system passes through the glass transition, segmental motions are slowed down, the reaction rate, controlled by these motions, is progressively reduced

and the unreacted reagents are trapped in the glassy matrix.

If indeed that is so, the weight increase during sorption may be the difference between the water sorbed and the low molecular weight component desorbed, so that data in fig. 2 may be misleading.

Water sorption on saturated-dried samples have been performed and reported in fig. 4 and 5 for 23° and 45°C, compared to "as prepared" samples (lower curves). The differences between the final asymptotic values is in both sorptions of the order of 0.5%, which supports the idea that desorption of the low molecular weight components takes place at same time as water in "as prepared" samples (it is indeed absent for saturated-dried samples).

At 45°C, fig. 5, the two processes appear to be equally as fast, since the two curves are well separated both in kinetics and equilibrium regions while at 23°C (fig. 4) desorption appears to be slower than water sorption. No such phenomena have been observed with the samples cured for 6 days, which did not exhibit any measurable weight loss when exposed to the preswelling-drying procedure. The sorption behaviour of samples as prepared and samples which had undergone the preswelling-drying procedure was identical.

These results suggest that 6 days curing at 100°C are required to completely cure the epoxy. 3 days final addet curing stage was not expected to improve mechanical properties and glass transition temperature values of the dry samples, since only 0.5% of the complete reaction was acheived, but to avoid "noise" in the sorption kinetics and equilibria determination.

Water sorption data of 6 days cured samples at 23°, 45°, and 75°C are reported in fig. 6 and 7 for thin and thick specimens respectively. In fig. 8, finally, sorption behaviour for 3 (dotted line) and 6 days (full line) cured epoxy is reported.

The kinetic appears to be adequately described by ordinary diffusion, since a finite initial slope is exhibed by sorption curves in the S vs $\sqrt{t/l}$ diagrams. Moreover, data obtained on films with varying thickness superimpose on such diagram (though the range of thickness investigated is not very wide: $0.40 \text{ mm} < l < 0.70 \text{ mm}$ and $2.00 \text{ mm} < l < 3.00 \text{ mm}$ for thin and thick samples respectively).

One can therfore extract a diffusion coefficient from the initial slope by making use of the early time approximation (15):

$$S/S_{\infty} = 4(Dt/2)^{\frac{1}{2}}$$

where S_{∞} is the asymptotic value of S and D is the diffusion coefficient.

Fig. 9 is an Arrhenius plot of diffusion coefficient obtained from the initial slope of fig. 6. A straight line has been drawn through the three data points, the corresponding activation energy for diffusion has been found to be 13.3 Kcal/mole.

Vapor sorption kinetics and equilibria

Sorption isotherm and sorption-desorption-resorption behaviour in very thin films (0.025 mm) have been investigated at 30°C for four Relative Humidity values.

Sorption desorption cycles have been run at low and high Relative Humidity values: 0.38 and 0.94 (reported as percent of 1). As for liquid sorption a S vs $\sqrt{t}/l$ diagram has been used. Figure 10 shows sorption-desorption-resorption kinetics for two different dry samples. Differences are not significant in the three different runs for each sample; neither sorption kinetics than equilibrium moisture contents are not affected by the previous history. Good linearity has been found in part of the diagrams S vs $\sqrt{t}/l$. At the first stages of the sorption (or desorption), however, a higher slope value (higher diffusion coefficient) has

been noted for both samples. Skin influence can be invoked to explain such a phenomena (15), its effects are, in fact, more important in so thin specimens.

Moisture desorption for R.H. changes from 0.94 to 0.68 and again to 0.31, fig. 11, have also run. In fig. 12 sorption isotherm is drawn through solubility data. A straight line well correlate experimental points. Absorptivity coefficient, defined as the slope in fig. 12, was found to be 3.20.

More work is in progress to investigate different temperatures.

Effects of hygrothermal history on water sorption equilibria: thermal spikes and sorption temperature changes

Thermal spikes: literature describes (1,4) as a hygrothermal cycling, simulating a "real life" of an epoxy in a particular application, can affect the sorption behaviour and the moisture equilibrium contents depending on the number of cycles, on the lower and upper spike temperatures, on the Relative Humidity and on other variables as thickness or thermal spike length. It is evident as the phenomenon is strickly related to

the combined effects of moisture content and thermal spikes. Thermal spike, per se, will not change sorption behaviour of an "as prepared" epoxy but its effects become dramatic when moisture is present in the polymer network.

In fig.13(1) water sorptions at 75°F of cycled and only immersed grafite-epoxy composite and resorption for cycled samples are compared. In the initial stages of the sorption both cycles and uncycled samples sorbe in the sale way while differences become evident and dramatic only when moisture content is graeter than 1%. Nevertheless such differences are evident for sorption in as prepared and resorption in cycled-saturated-dried samples, heither for kinetic and equilibrium moisture content. No differences are reported by the authors in the same paper for sorption and resorption of the only immersed in water samples.

Further tests (1) also confirmed that the thermal spike permanently increase the value of the material absorptivity coefficient, owing to assume that irreversible fenomena have been occurred.

A series of arbitrary thermal spikes on saturated thin (0.5 mm) epoxy resin sheets have been run. In fig. 14 thermal cycle and sorption behaviour are reported as functions of time. Sorption test temperature

of 90°C and upper and lower spike temperatures of 150 and -20°C have been arbitrarily chosen. Spike lengths of 1 hr have been used.

The effects on moisture contents of such a cycle, reported in fig. 14, are not evident. Probably, for 0.5 mm thick samples, 1 hr spike is too long. The resulting annealing at 150°C (the glass transition temperature of our dry epoxy is 135°C) will allow the system again in the "as prepared" state and then it will sorbe, at that temperature, the same amount of moisture. Spikes on the same system performed using 120°C as upper temperature of the thermal cycle gave similar results.

Experiments to find as long is long for defined sample thickness are in progress, since the spikes effects are evident only for short length cycles.

Sorption temperature changes: a reproducible and well defined temperature history influence on water sorption in epoxy resins has been determined experimentally.

While solubility values at 23° and 45°C are not significantly different, the value at 75°C is certainly higher than the other two (see fig. 6). One would therefore expect that a sample brought to equilibrium at 75°C, would exhibit water desorption if brought, after that, to 23°C.

When this experiment was performed, however, the opposite behaviour was observed as shown in fig.15. After the sample has apparently reached equilibrium at 75°C, when brought down to 23°C significant additional sorption of water takes place. The new value of the apparent solubility at 23°C is 4.86%, as compared to 3.92% observed in the virgin samples.

Figure 16 shows, on an expanded scale, the additional sorption at 23°C of a sample previously equilibrated at 75°C (open circles). When the same sample is brought back to 75°C water desorption takes place and the final apparent solubility is the same as that of a virgin sample, i.e., 4.12%.

If a sample is first equilibrated at 23°C, then at 75°C, and again at 23°C, its behaviour (full circles) is the same as that of a sample just equilibrated once at 75°C. It appears that the only relevant parameter of the hygrothermal history of the sample is the highest temperature at which it has been equilibrated in to water.

Figure 17 reports data similar to the one in fig. 16, and relative to a 75°-45°-75°C cycle. The apparent solubility at 45°C of a sample previously equilibrated at 75°C (4.60%) is significantly larger than that of a sample saturated at 45°C (3.90%).

Figure 18, reports the same type of data for a 45° - 23° - 45° C cycle; again the same kind of behaviour is observed.

The experimental results discussed so far clearly indicate the existence of a hygrothermal history influence on apparent sorption equilibria. Such history-dependent equilibria have been discussed in the literature (5, 6, 7), and it has been suggested, also in more general terms, that history-dependent thermodynamics may be approached from the viewpoint of internal, or hidden, state variables (16, 17). Specifically, we may assume that the state of the samples identified, in addition to the state variables, also by at least one additional state variable x .

For the phenomena considered here, a concrete physical interpretation for the internal state variable x may be suggested: x may be regarded as the volume percent of microcavities which may form in the sample under the combined action of temperature and humidity. This specific identification of x , however, is not crucial to the subsequent analysis, and although we will refer to microcavities volume percent in the following, we do not claim to have definite experimental proof that indeed such microcavities do form, though physical support for this kind of interpretation of x

is discussed below.

The apparent solubility in a given sample, S_{∞} , may be regarded as the sum of two terms, the first one, S_p , representing the equilibrium content of water in the compact resin, and the second one, proportional to x , representing the amount of water which may be present in the microcavities:

$$S_{\infty} = S_p + \beta x$$

Since the densities of water and of the saturated system are very close to each other, the value of β is approximatively unity, and will be take as unity in the following.

Assuming that in a vergin sample $x = 0$, further more that the rate of formation, dx/dt , is neglegible at 23°C, and is sufficiently fast at 75°C, so that while sorption proceeds to apparent equilibrium the value of x also reach some equilibrium value x_{75} , a sample previously equilibrated at 75°C is characterized by a value $x=x_{75}$, while a virgin sample is characterized by $x=0$. Comparison of the 23°C enties in the second and third column of table 1, were are reported the value of S_{∞} for virgin samples first equilibrated at 75°C, allows to estimate the value of x_{75} as 0.94%. A similar analysis on S at 23°C for virgin and first equilibrated at 45°C samples yields for x_{45} , the equilibrium microca

vities volume fraction percent at 45°C, the value of 0.27 (see fifth column in tabke 1).

It may be observed that a defined decreasing trend is observed with increasing temperature for the calculated values of S_p reported in the sixth column of table one, while no such regular tend is observed for the entries in the second column, where S_{∞} values are reported.

An alternative interpetration can be suggested from previous literature (5, 6, 7) on relaxation phenomena occuring in the swollen state. Samples allowed to be saturated in water at high temperatures can show a more relaxed glassy state as compared to that of samples saturated at low temperatures. In the more relaxed state additional water sorption can take place when water environment is cooled down to a lower temperature. In both cases, howevern an exothermic sorption behaviour is observed.

The tentative interpretation based on microvoids formation would need of course to be subjected to scrutiny. The following points are offered ad support.

- 1) The differences between the two values of x at 75°C and at 45°C (0.95 and 0.27% respectivly) is 0.67%. This compare very favorably with the different apparent solubilities at 45°C observed in the 45°-75°-45°C cycle:

4.60%-3.90% = 0.70%.

2) Nodular structures have been observed in epoxy systems (3, 18). Sites with high and low cross-linking densities can induce stress concentration during the swelling do to the moisture sorption.

3) Stress induced crazing in epoxy resins and in various systems has been reported in literature (3, 19, 20); furthermore the energy required for the crazes formation is known to decrease with increasin temperature (20,21). Therefore the interpretation based on formation of microcavities, which is favoured by higer temperatures, is in agreament with available information.

4) A sample previously equilibrated at 75°C, dried at temperature above T_g , exhibits the same sorption behaviour of a "as prepared" sample. It is indeed physically intuitive that any crazes which may have formed would disappear through the annealing process.

5) Weight gains greater than equilibrium amounts were observed (4) without accompanying T_g changes which was attributed (4) to moisture entrapment during microcracking in the resin.

Other points will be offered as support in the following.

Stress-strain behaviour for dry samples

Stress-strain curves for 6 days cured dry epoxies, reported in fig. 19, refer to 23°, 75°, 90°, 110°, 130°, 150°C. Brittle behaviour has been observed at 23°, 75°, and 90°C, ductile, ductile-rubbery and rubbery behaviour were observed at 110°, 130° and 150°C respectively. Such a behaviour is consistent with shear modulus decay observed in fig. 1. At low temperature and until 100°C, significative percentage changes were not, in fact, observed for shear modulus values and then the brittle behaviour is maintained; from 90° to 120°C decay starts to be evident and a ductile behaviour can be observed in the s-s tests; from 120° to 125°C a dramatic modulus fall allows the system to a ductile-rubbery state while above 135°C a completely rubbery state is reached.

Figure 20 shows in a linear scale ultimate tensile properties as function of temperature. In the upper part of fig. 20 elastic moduli E , expressed in Kg/cm^2 , is reported while ultimate elongation and stress are reported in the lower part of the same.

Effects of water sorption on s-s behaviour

Stress-strain tests on saturated samples (cured 6 days) have been run at same temperature at which sorption was carried out. Tests have been run in water environment to avoid moisture desorption.

In figures 21, 22 and 23 s-s curves for dry and saturated samples are compared, respectively at 23°, 45° and 75°C. The presence of a diluent is evident in a plasticization effect. Elastic moduli and σ_b are in all cases lowered of about 20% of the dry value. Stress-strain curves at different temperatures can not be compared since different amount of moisture are present in the three system.

Moreover an other point is added as support for microcavities interpretation of sorption behaviour in the following.

Stress-strain mechanical tests on dry and previously saturated at 75° and 45°C samples have also been performed. At temperature of 75°C, fig. 24, a brittle behaviour for dry and 75°C saturated samples and a ductile behaviour for 45°C saturated sample has been observed, in accordance with the solubility values, S_p , of table 1. The more plasticized (the sample saturated at 45°C, which shows a ductile behaviour in

fig. 24) has, in fact, in table 1 a value of S_p higher than that of a 75°C saturated sample. Conversely an opposite behaviour should be observed if S_∞ were assumed as true solubilities.

Effects of water sorption on shear moduli and Glass Transition Temperatures

Clash-Berg mechanical tests have been performed on samples previously saturated with water at temperatures of 75°, 45° and 23°C. The results are reported in fig. 25 and 26, for 3 and 6 days cured samples, compared with the shear moduli of dry samples. One can notice that shear modulus drop above T_i (initial glass transition temperature as defined in fig. 1) takes place for dry samples within a small range of temperature while it became larger for saturated samples. This can be interpreted as favoured water desorption from the samples during test times, above the initial glass transition temperature. Water desorption at temperature below T_i can be assumed to be negligible related to the still glassy state of the system. This assumption seems to be confirmed by the fact that T_i for the dry system as for those saturated at 75°, 45° and 23°C are well separated in the temperature scale while T_f , final glass transition

temperatures, are quite coincident (fig. 25). Glass transition temperatures for saturated samples, reported in table 2, can be then calculated as $T_i + \Delta T/2$, where ΔT is the value $(T_f - T_i)$ calculated for dry system from fig. 1. In the case of 23°C saturated samples, both for 3 and 6 days cured samples, T_i can not be extracted from fig. 25 and 26 because a continuous decreasing trend is observed for shear modulus values. Such a trend is the result of an antiplasticization effect (22, 23, 24), fig. 27 (24), complicated by the described moisture desorption during the test and for which hardness maximum values for particular concentration while monotonically decreasing softening point with increasing plasticizer concentration can be found.

Moreover for 3 days cured samples, fig. 25, as for 6 days cured samples, fig. 26, shear modulus values below T_i are not well distinct each other in the region 25-50°C, depending on the antiplasticization effect previously described. Antiplasticization on the three saturated samples will be more evident in C-B. run from lower temperatures. Although the differences in the absolute values of the shear moduli for 3 and 6 cured resins, glass transition temperature, calculated as $T_i + T/2$ are well coincident for 45° and 75°C saturated samples (see table 2).

Again it may be observed that the samples saturated at 45°C show a lower glass transition temperature than those of samples saturated at 75°C, in spite of the more plasticized state that can be expected (25, 26) because the value of S_{∞} at 45°C (3.90%) is less than the value at 75°C (4.12%). Yet, if indeed microcavities are formed, one would expect that only the water actually dissolved in the compact resin (value of S_p), is responsible for the plasticization action; and indeed the value of S_p at 45°C (3.63%) is larger than the value at 75°C (3.18%). Finally the largest value of x reported in table 1 is 0.94%; such a value is not expected to significantly change the mechanical properties: the shear modulus would only decrease of about 3% (27), well below the experimental accuracy.

CONCLUSIONS

A reproducible and well-defined temperature history influence on water sorption in epoxy resins has been determined experimentally; tentative interpretations of the effect on the basis of microcavities formation have been suggested.

Experiments are in progress on the effects of stresses and relative humidity on the sorption kinetics and mechanical properties of the epoxies. Also permeability studies on thin epoxy films under high applied pressure have been started.

REFERENCES

- 1) E.L. Mc Kague, Jr, J.E. Halkias, J.D. Reynolds, J. Composite Materials, 9, 2, (1975).
- 2) Chi-Hung Shen, G.S. Springer, J. Comp. Mat., 10, 2 (1976).
- 3) R.J. Morgan, J.E.O'Neal, Pol. Pla. Thechnol. Eng., 10, 49, (1978).
- 4) C.E. Browing, Pol. Eng. Sci., 18, 16 (1978).
- 5) A.R. Berens, Polymer, 18, 697 (1977).
- 6) D.J. Enscoe, H.B. Hopfenberg, V.T. Stannett, A.T. Berens, Polymer, 18, 1105 (1977).
- 7) A.R. Berens, H.B. Hopfenberg, Polymer, 19, 489, (1978).
- 8) ASTM D 1043-61T.
- 9) K.H. Illers, Makromol. Chem., 127, 1, (1969).
- 10) D.L. Faulkner, H.B. Hopfenberg, V.T. Stannett, Polymer, 19, 489 (1978).
- 11) A. Apicella, E. Drioli, H.B. Hopfenberg, E. Martuscielli, L. Nicolais, "The Effect of Thermal treatment, Residual Solvent and Preswelling on the Thermal Properties and Sorption Behaviour of PPO-PS Blends", Pol. Eng. Sci., in press.
- 12) S. Lunak and J. Vladika, Polymer, 19, 931 (1978).
- 13) Hovic, K., H. Sawada, M. Mita, I. and Kambe, H., J. Pol. Sci., 8, 1357 (1970).
- 14) Babayesky, P.G. and Gillham, J.K., J.A. Pol. Sci., 17, 2067 (1973).
- 15) J. Crank, "The mathematics of diffusion" second edition, Oxford press.

- 16) G.C. Sarti, G. Astarita, Trans. Soc. Rheol., 19, 215 (1975).
- 17) F. Astarita, G.C. Sarti, Pol. Eng. Sci., 16, 490, (1976).
- 18) J.L. Racic, J.A. Koustky, J.A.P.S., 20, 2111, (1976).
- 19) E. Drioli, L. Nicolais, A. Ciferi, J. Pol.Sci. (Pol. Chem. E1) II, 3327, (1972).
- 20) E.H. Andrews, L. Bevan, Polymer, 13, 337 (1972).
- 21) E.H. Andrews, G.M. Levy, J. Willis, J. Mat.Sci., 8, 1000 (1975).
- 22) Jackson, W.J. Calwell J.R., J.A.P.S., 11, 221 (1967).
- 23) Naoki Hata, JU Kumanotani, J.A.P.S., 21, 1257 (1977).
- 24) Mascia L., Polymer, 19, 325, (1978).
- 25) F.N. Kelly, F. Bueche, J. Pol.Sci., 50, 549 (1961).
- 26) H.G. Carter, K.G. Kilber, J. Composite Material, 11, 265 (1977).
- 27) L.E. Nielsen, "Mechanical properties of polymer and composites", Marcell Dekker, Inc., N.Y., vol. 2, 387 (1974).

T A B L E 1

THE EFFECT OF TEMPERATURE AND PRIOR HISTORY ON THE APPARENT SORPTION EQUILIBRIA

Temperature °C	S_{∞} for Virgin Sample, %	S_{∞} for Sample first equilibrated at 75°C, %	S_{∞} for Sample first equilibrated at 45°C, %	Calculated Volume void Fractions, %	Calculated " S_p ", %
23	3,92	4,86	4,15	0	3,92
44	3,90	4,60	3,90	0,27	3,63
75	4,12	4,12	-	0,94	3,18

T A B L E 2

Samples	T _g , °C for 3 days cured samples	T _g , °C for 6 days cured samples	S _p , %
Dry	135	135	0.0
Saturated at 75°C	108	108	3.18
Saturated at 45°C	88	91	3.63

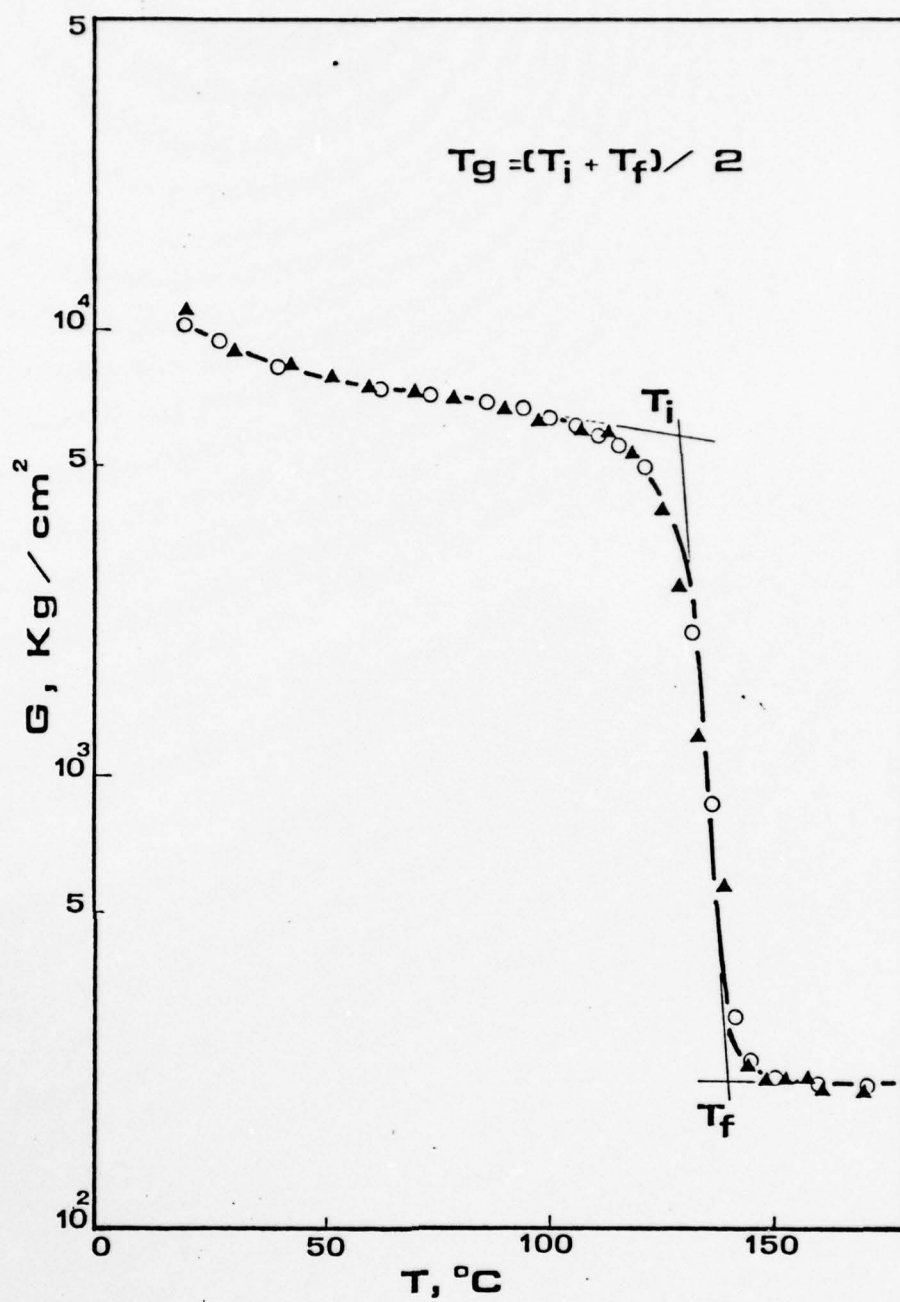


Fig.1) Torsional test results for dry samples. Triangles: 6-days cured samples.
Circles: 3-days cured samples.

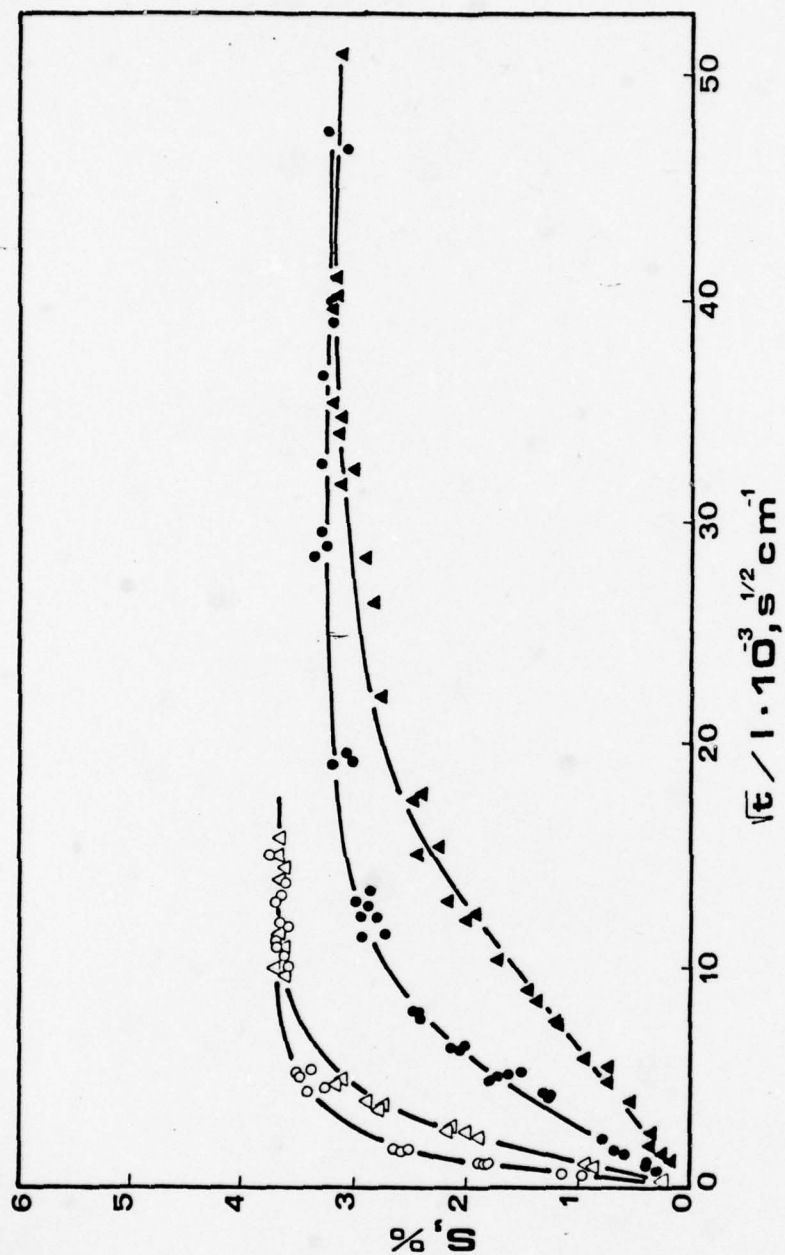


Fig.2) Sorption behaviour of 3-days cured samples, as prepared. Thin specimens.
Solid triangles: 23°C. Solid circles: 45°C. Open triangles: 75°C. Open circles: 90°C.

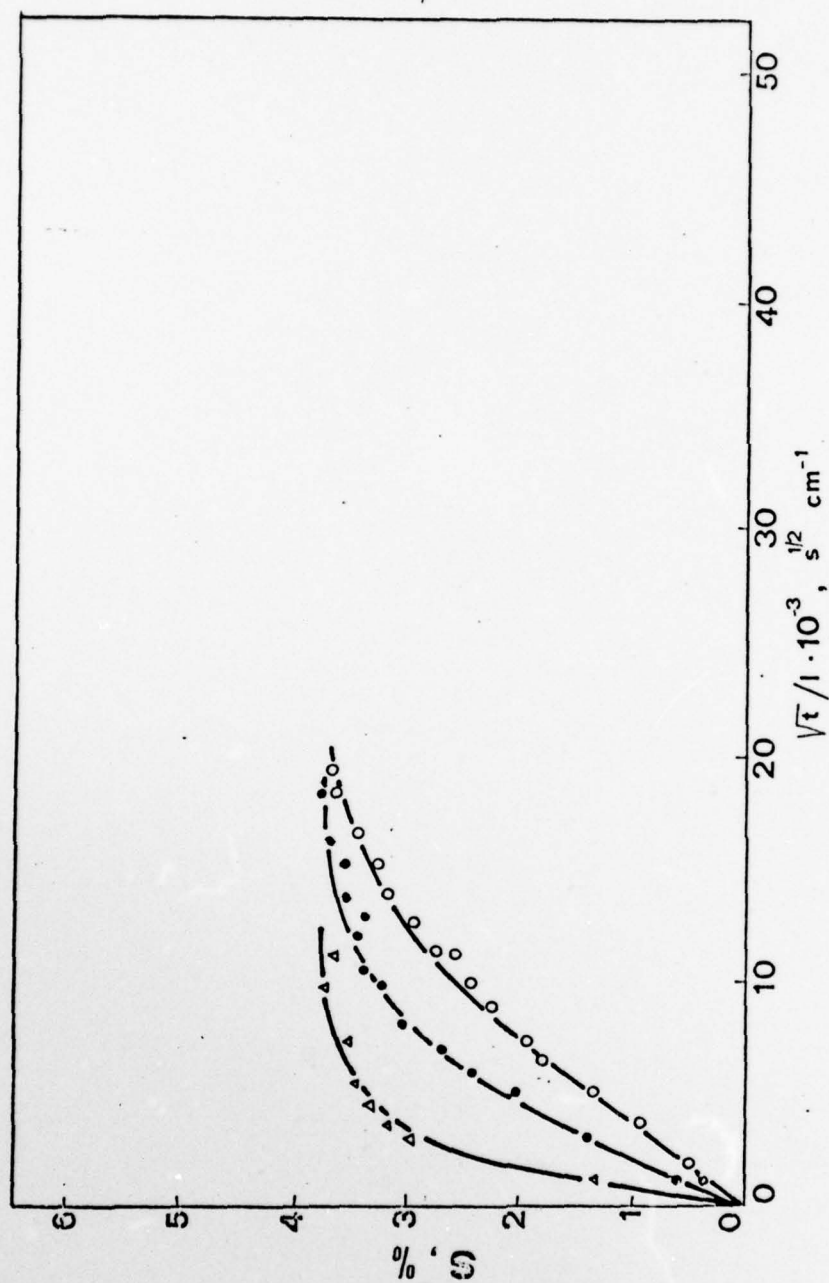


Fig.3) Sorption behaviour of 3-days cured samples, as prepared. Thick specimens.
Open circles: 23°C. Solid circles: 45°C. Open triangles: 75°C.

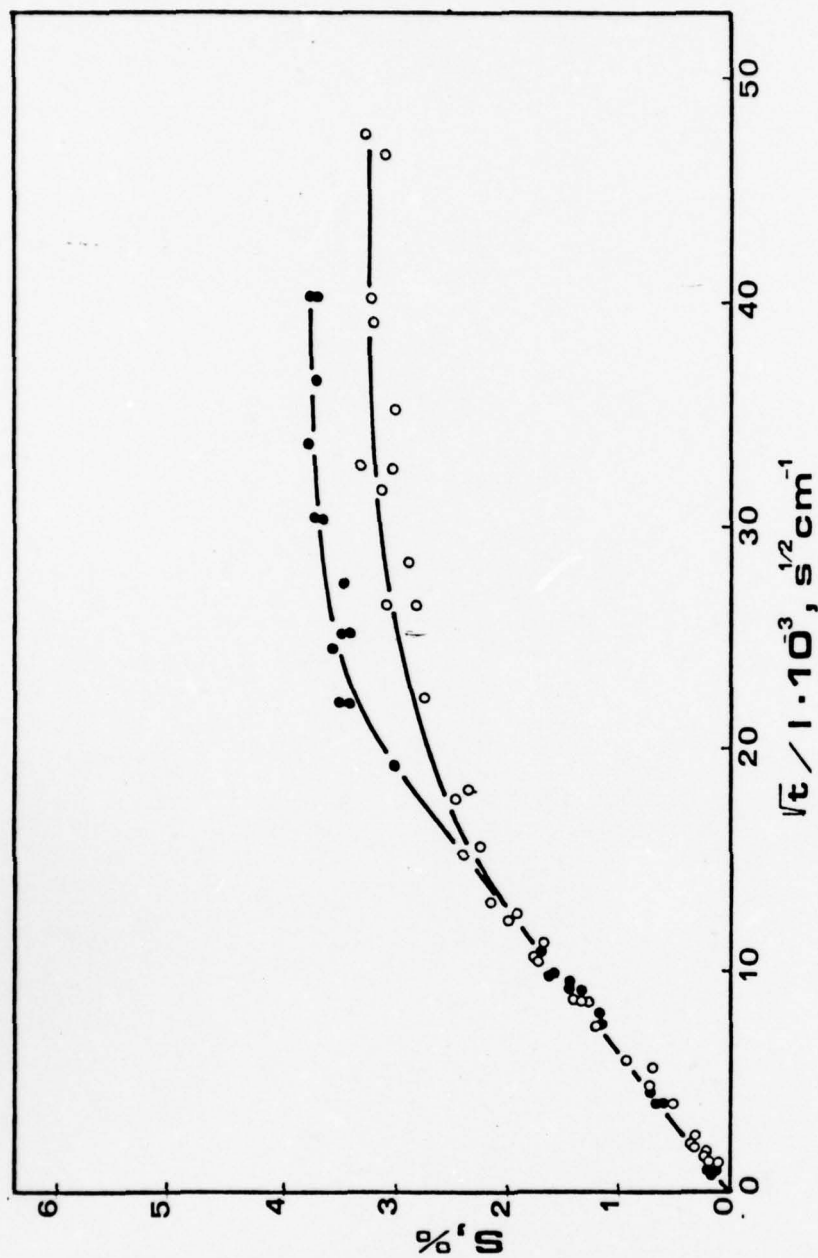


Fig.4) Sorption behaviour at 23°C for 3-days cured samples (thin).

Open circles: samples as prepared. Solid circles: samples previously swollen and dried.

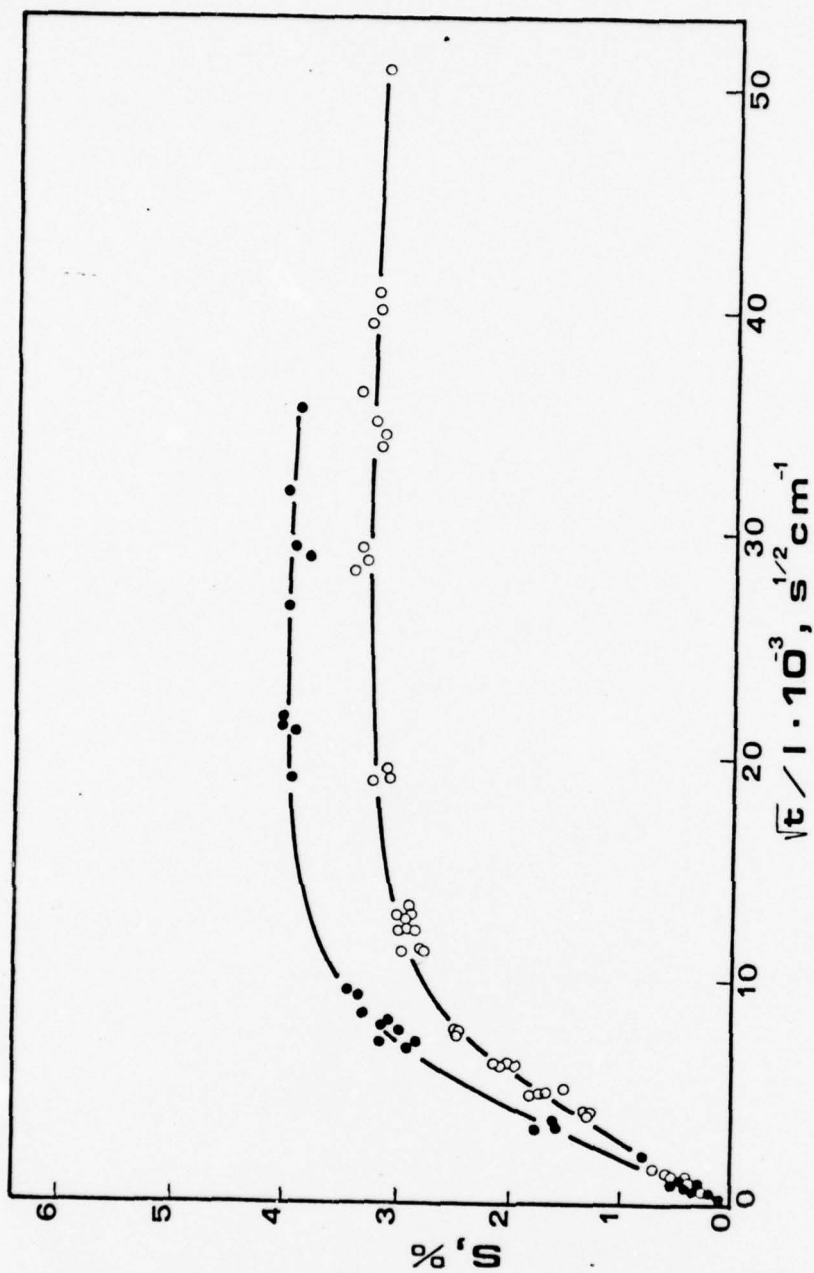


Fig.5) Sorption behaviour at 45°C for 3-days cured samples(thin). Kev as in Fig.4.

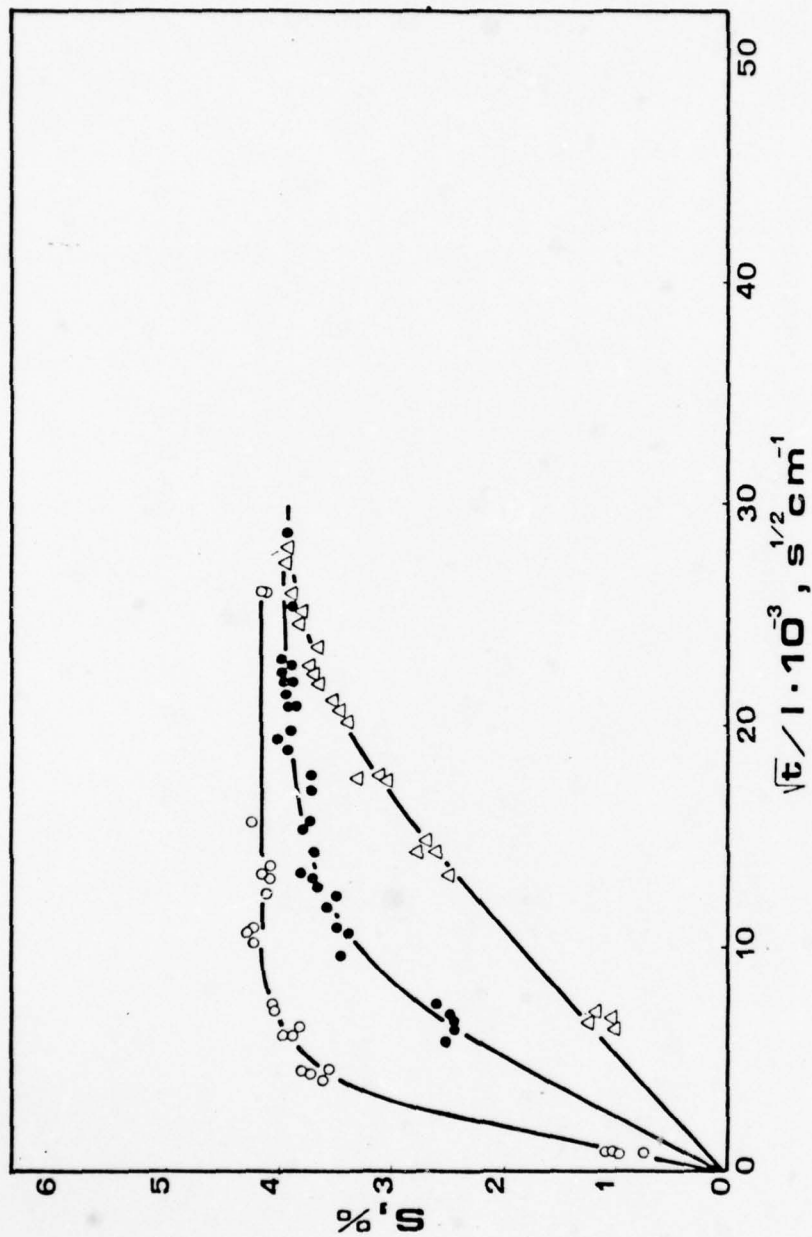


Fig.6) Sorption behaviour for 6-days cured samples. Thin specimens. Open triangles: triangles: 23°C. Solid circles: 45°C. Open circles: 75°C.

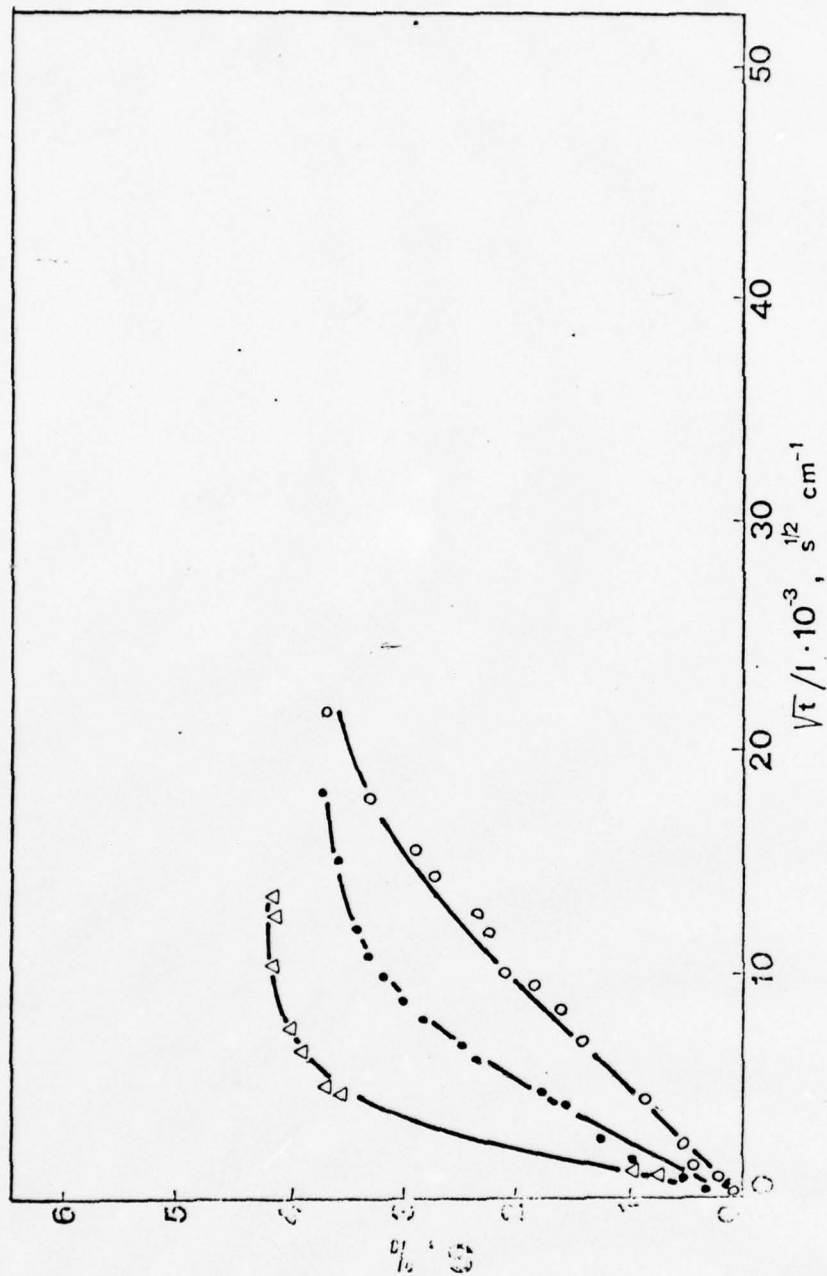


Fig.7) Sorption behaviour for 6-days cured samples. Thick specimens. Open circles: 23°C. Solid circles: 45°C. Open triangles: 75°C.

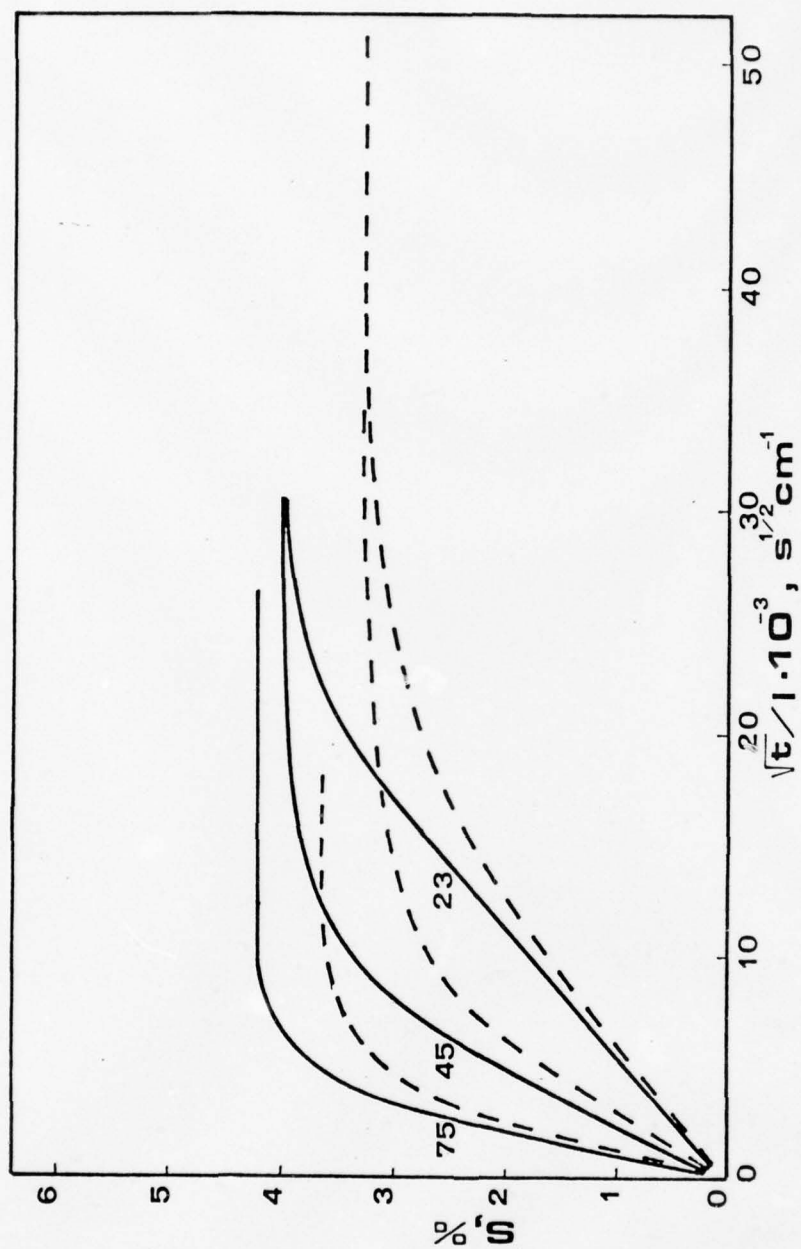


Fig.8) Comparison between sorption behaviour for 3 and 6-days cured samples.
Dotted line: 3-days cured. Full line: 6-days cured.

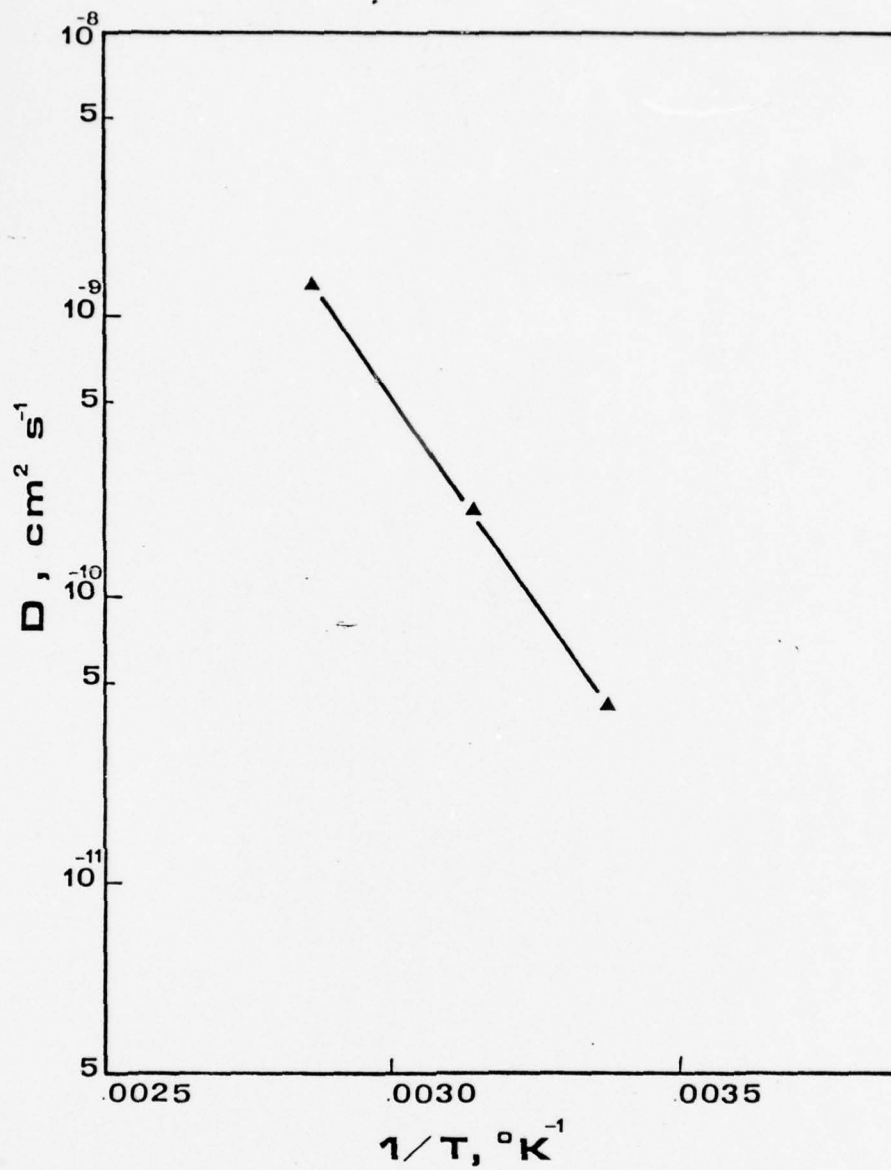


Fig.9) Arrhenius plot for diffusivities extracted from Figure 6.

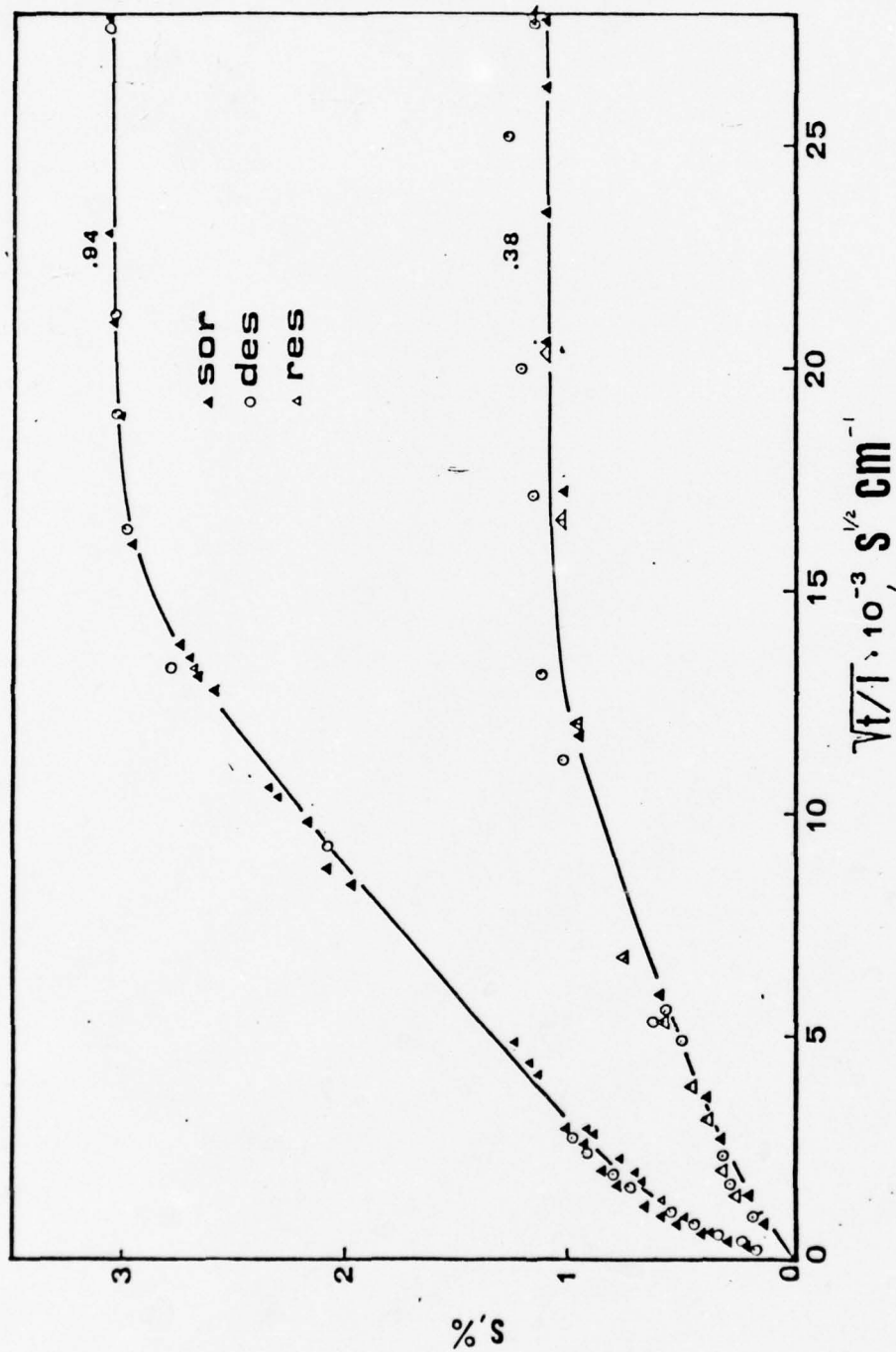


Fig.10) Sorption-desorption-resorption from vapour phase at different Relative Humidities, $T = 30^{\circ}\text{C}$.

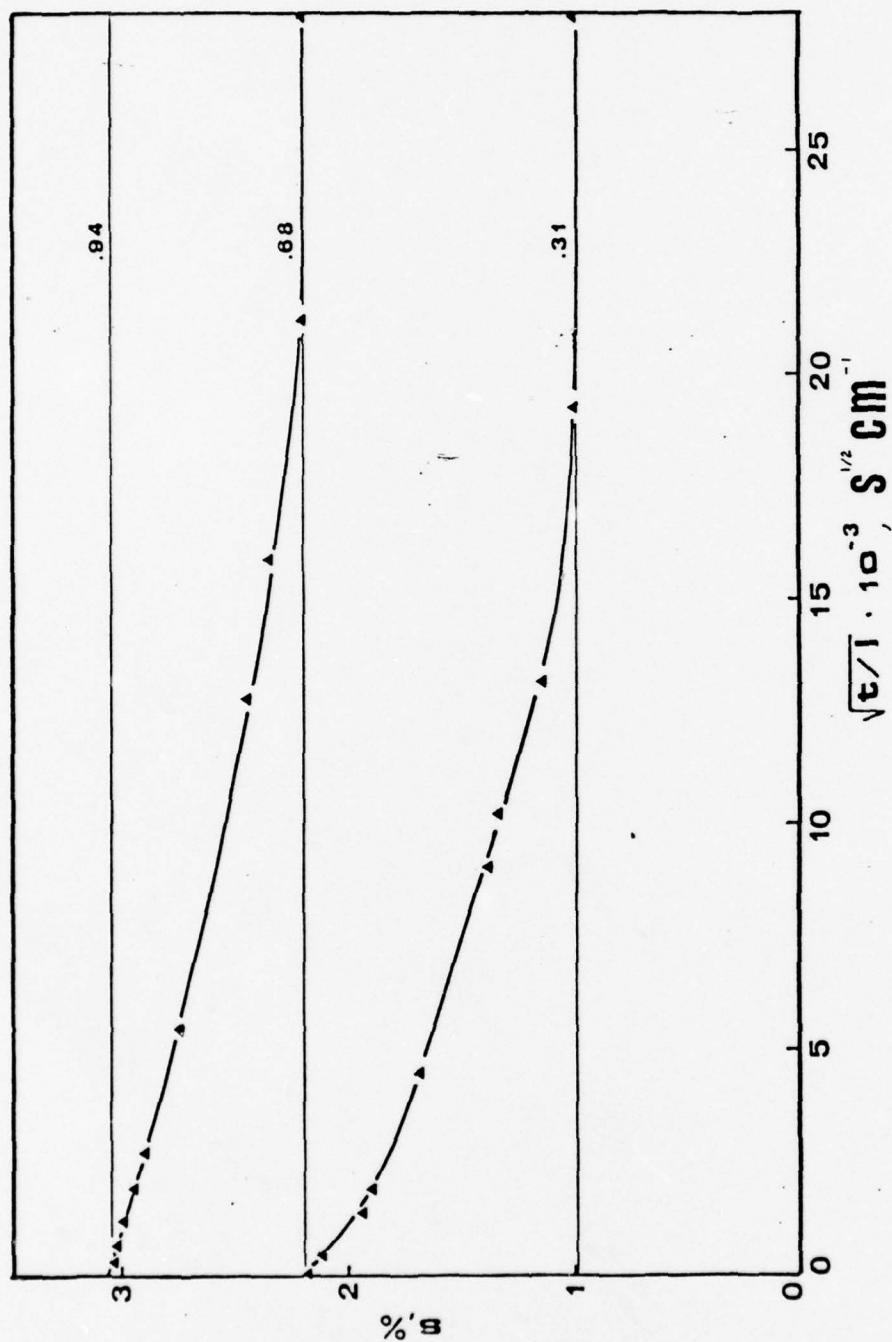


Fig.11) Desorption behaviour for R.H. changes, $T = 30^{\circ}\text{C}$.

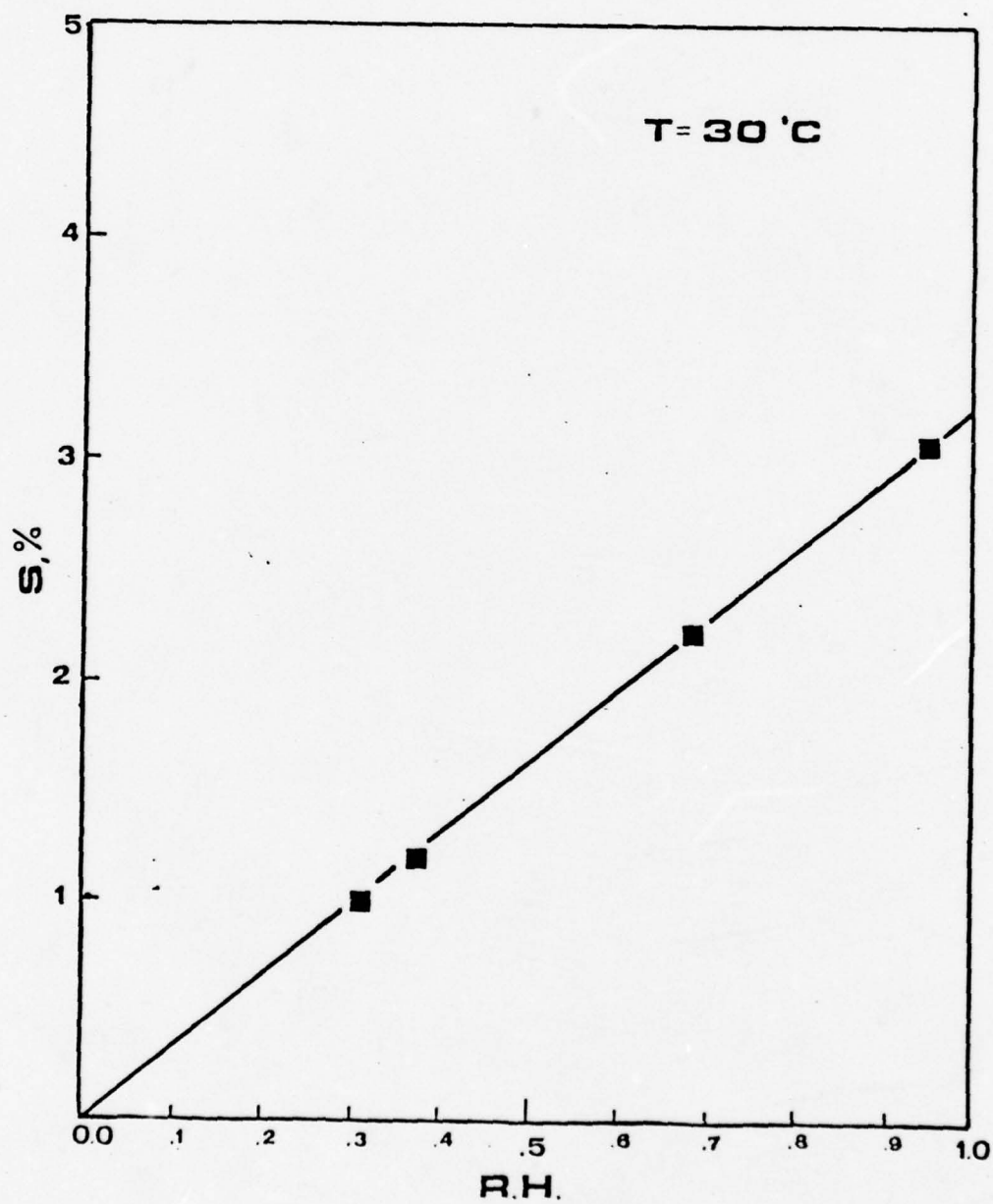


Fig.12) Isotherm equilibrium sorption values as function of R.H., $T=30^{\circ}\text{C}$.

THE MATERIAL IS PERMANENTLY CHANGED BY
SUPERSONIC FLIGHT CONDITIONS

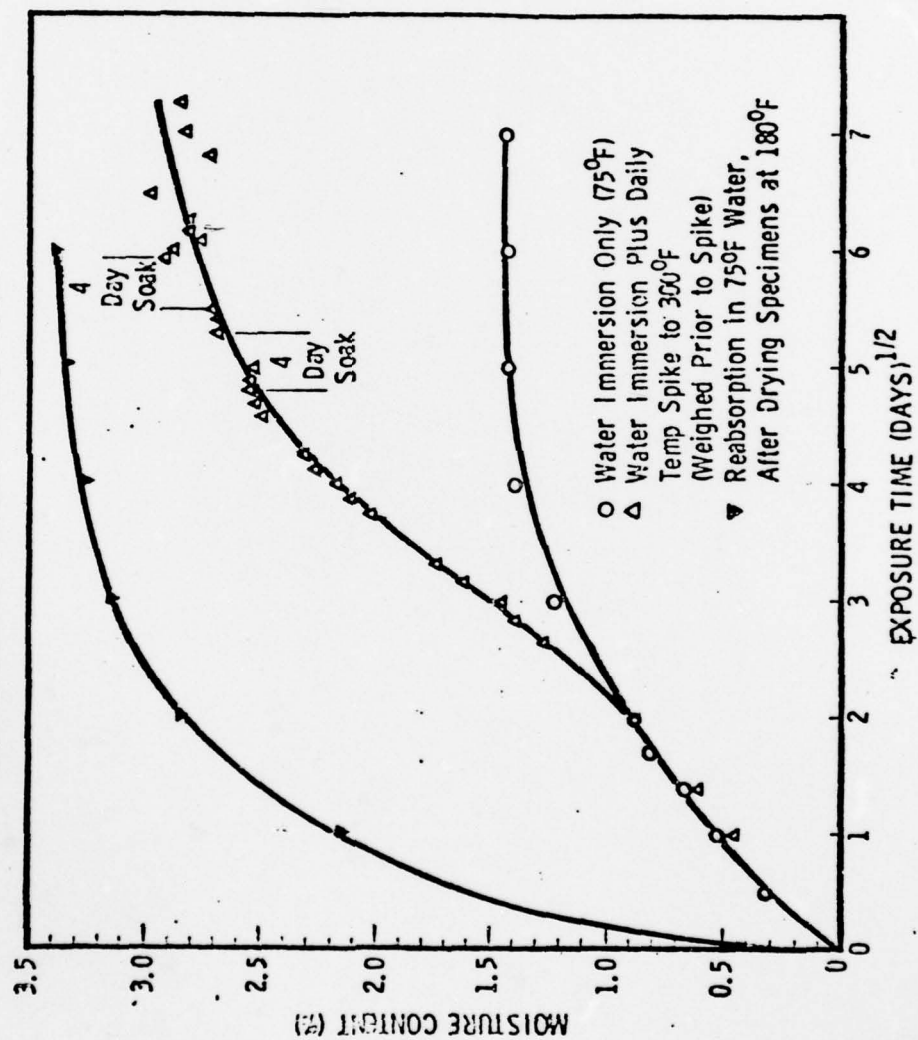


Fig.13) Changes occurring in a material exposed to supersonic fly condition(1).

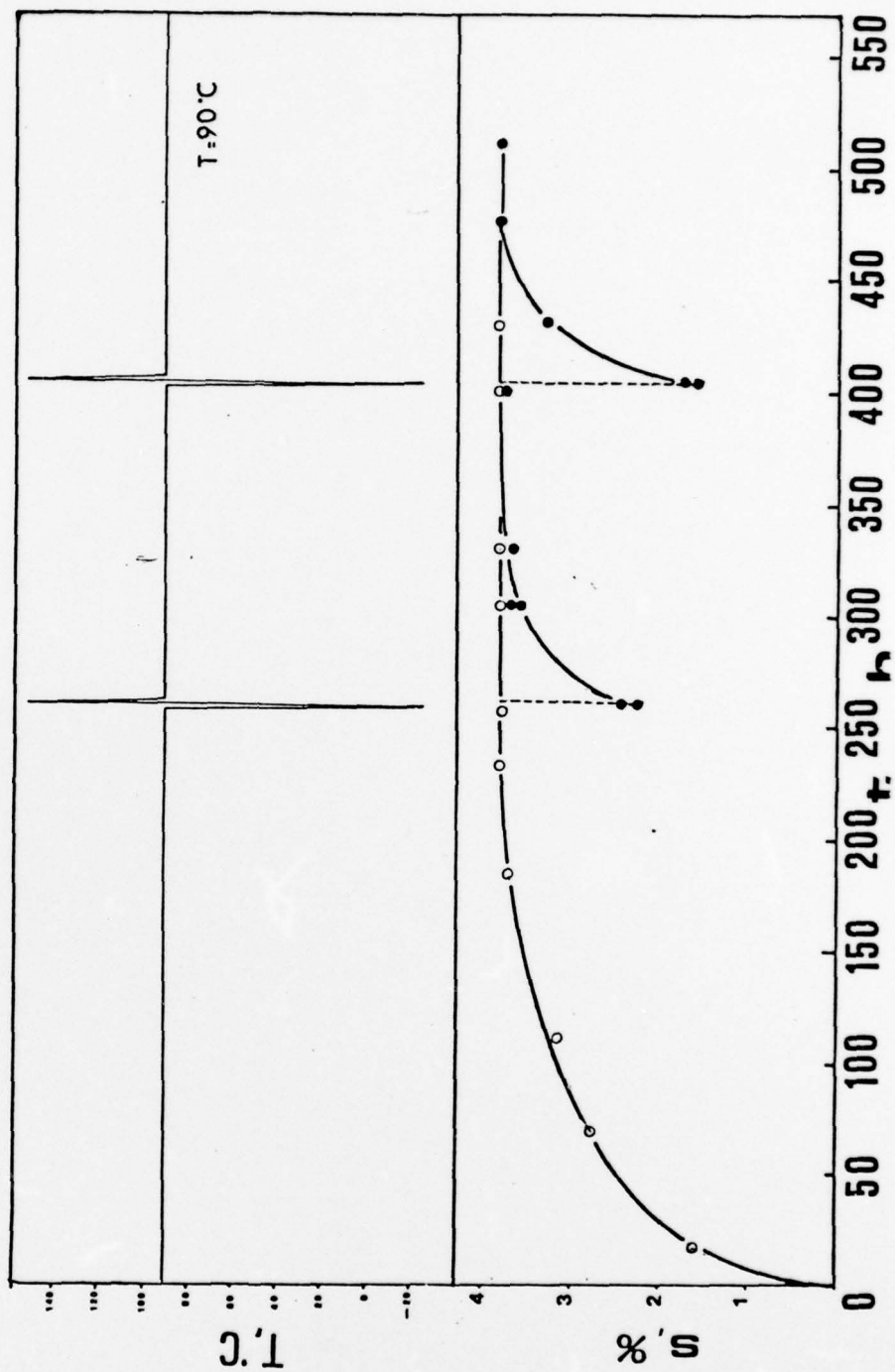


Fig:14) Thermal spikes and their influence on sorption behaviour at 90°C .
 Open circles: reference samples. Solid circles: cycled samples.

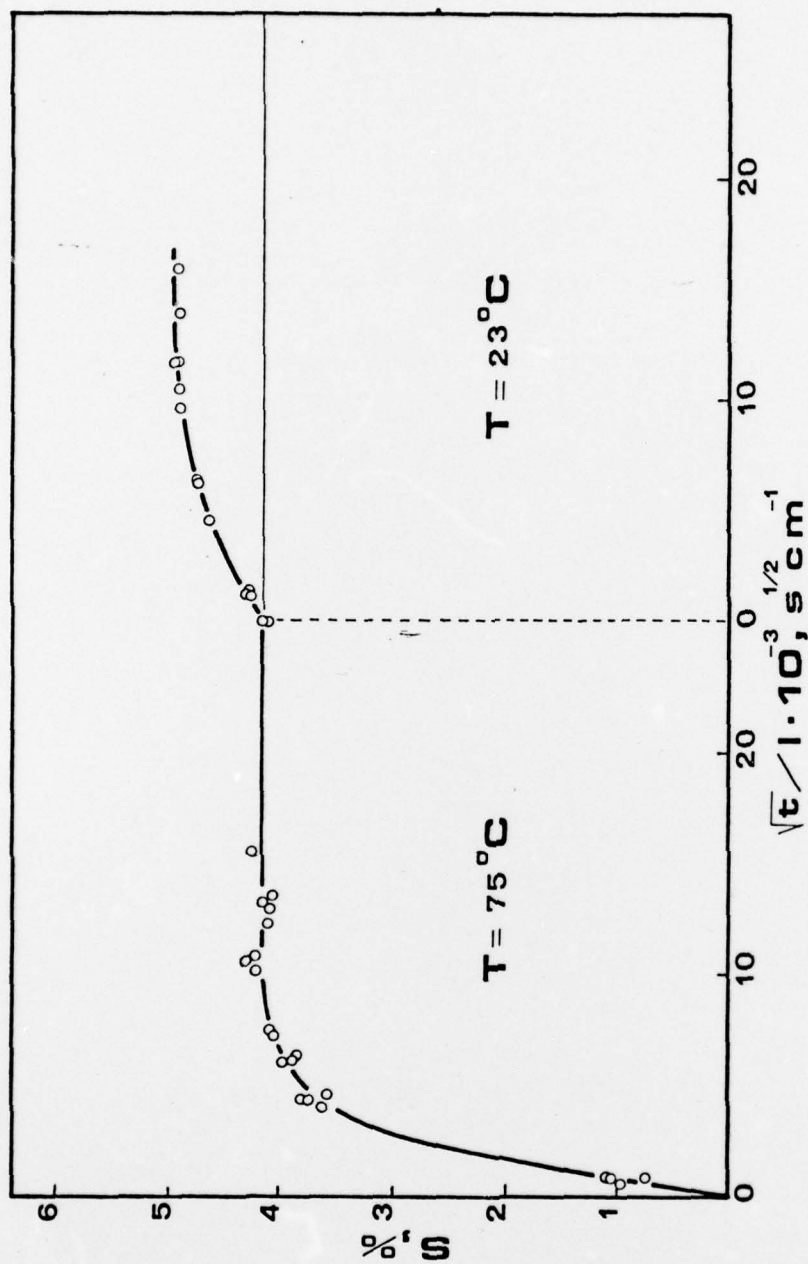


Fig.15) Sorption behaviour at 23°C(right half) of samples previously equilibrated at 75°C(left half).

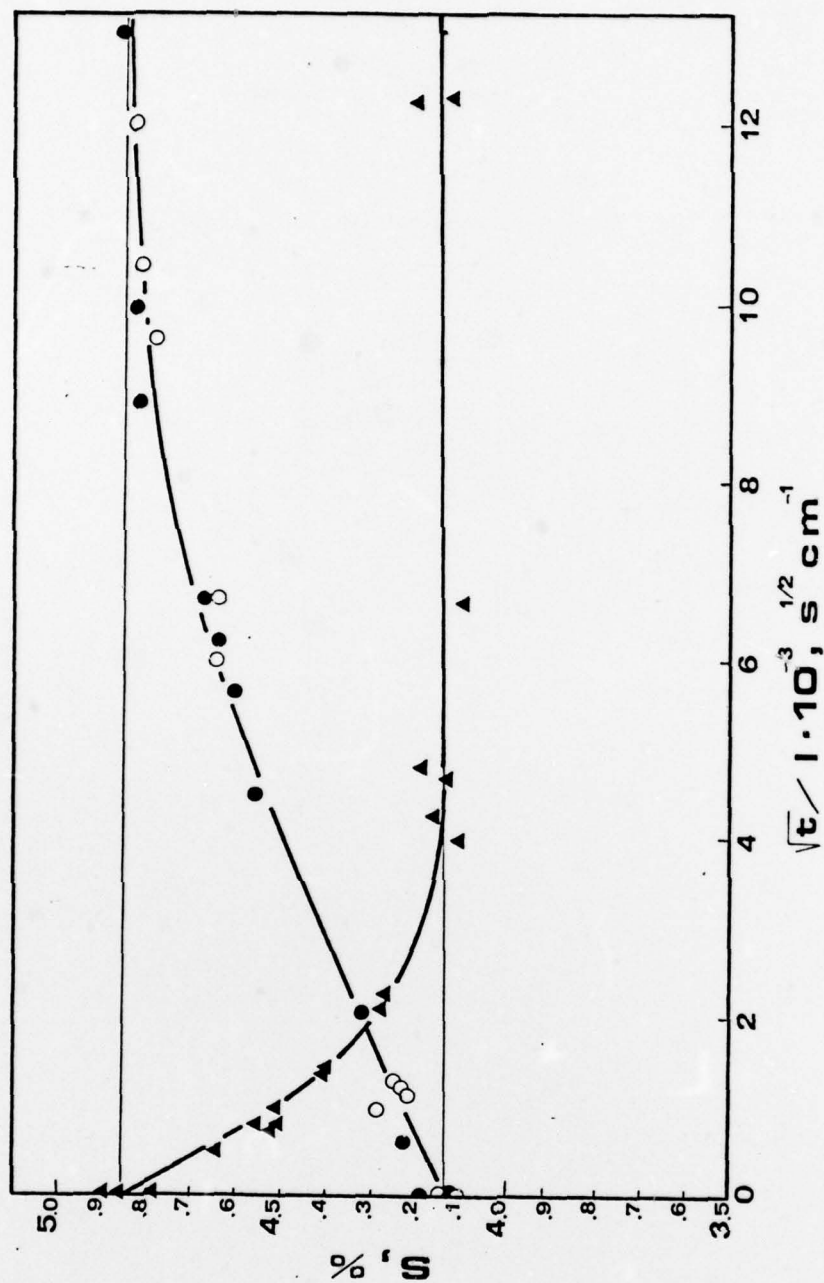


Fig.16) Sorption behaviour at 23°C of samples previously equilibrated at 75°C (open circles). Desorption when brought back to 75°C(triangles). Sorption at 23°C with different hygrothermal history, see text(solid circles

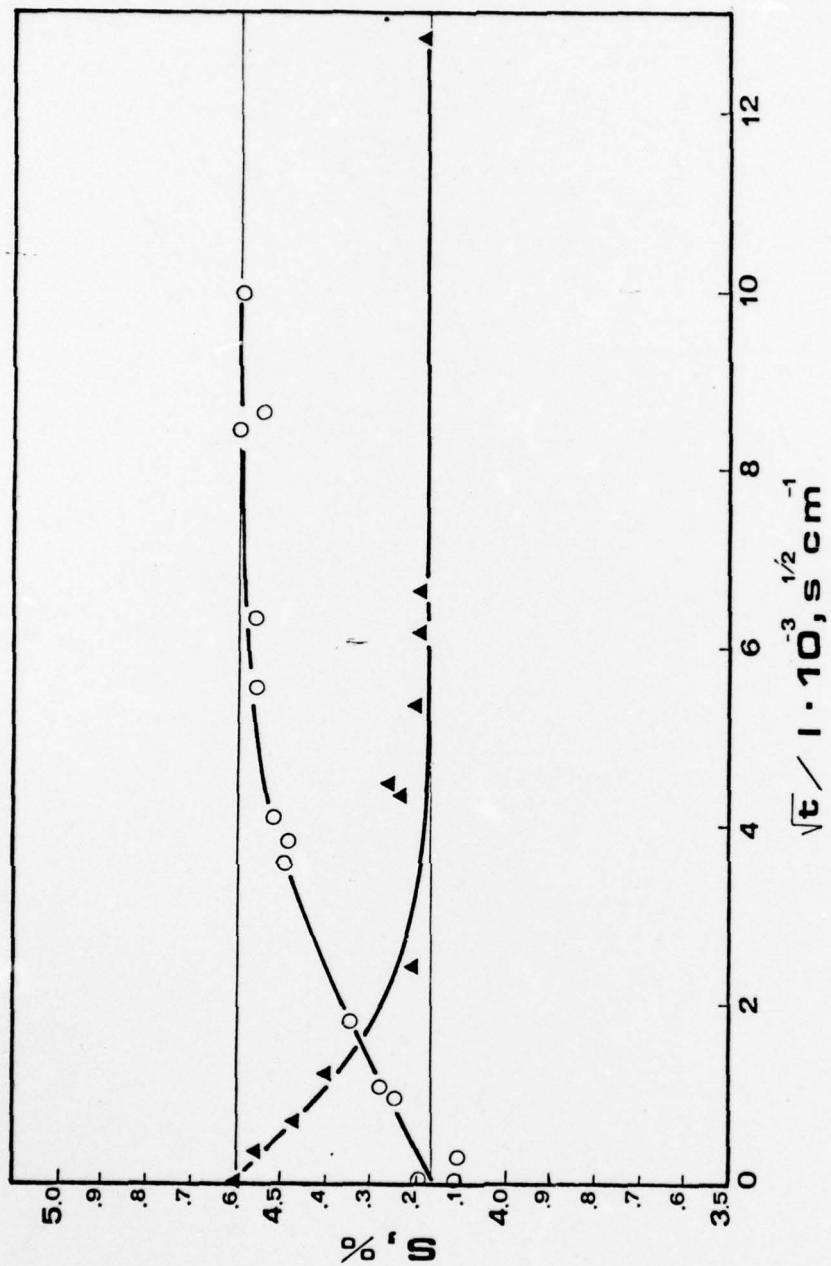


Fig.17) Sorption at 45°C of samples previously equilibrated at 75°C(circles).
Desorption when brought back to 75°C(triangles).

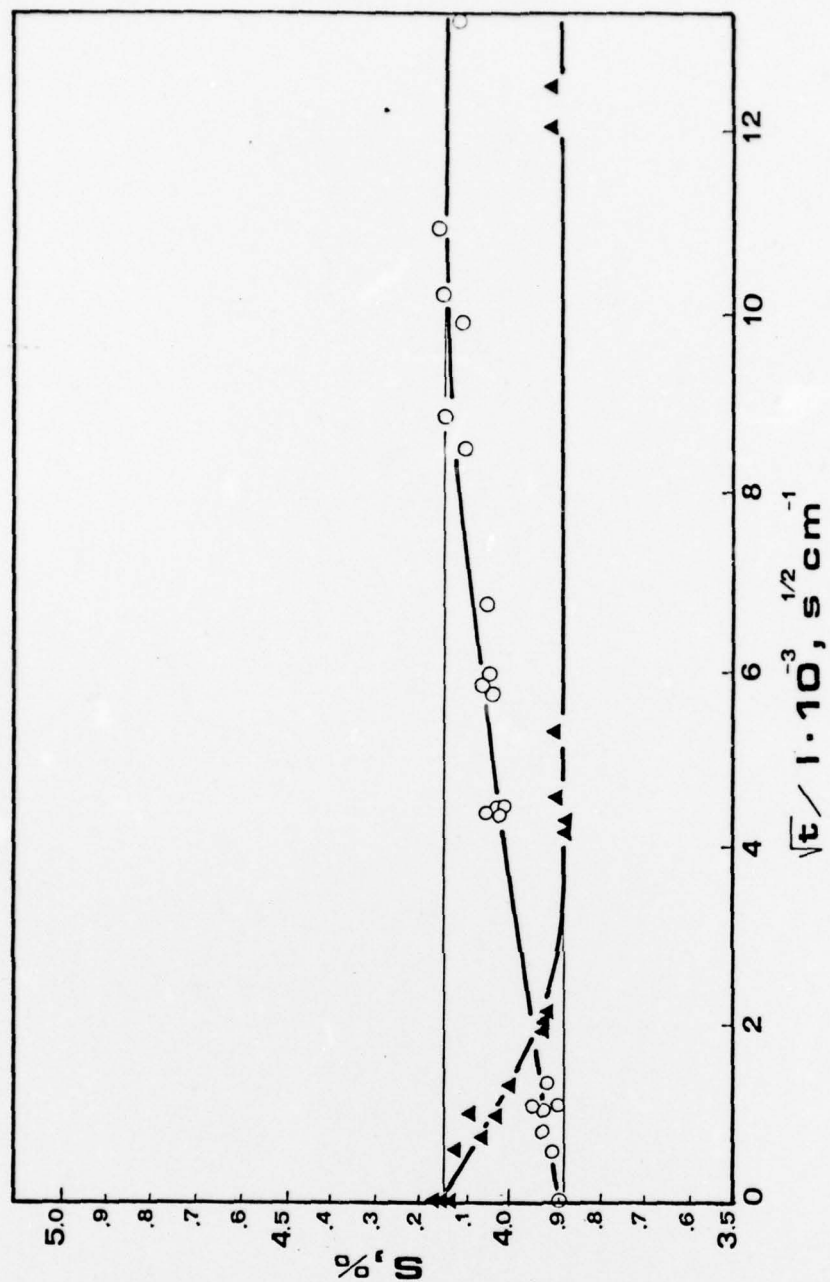


Fig.18) Same as figure 17 for a 45°-23°-45°C temperature cyclig.

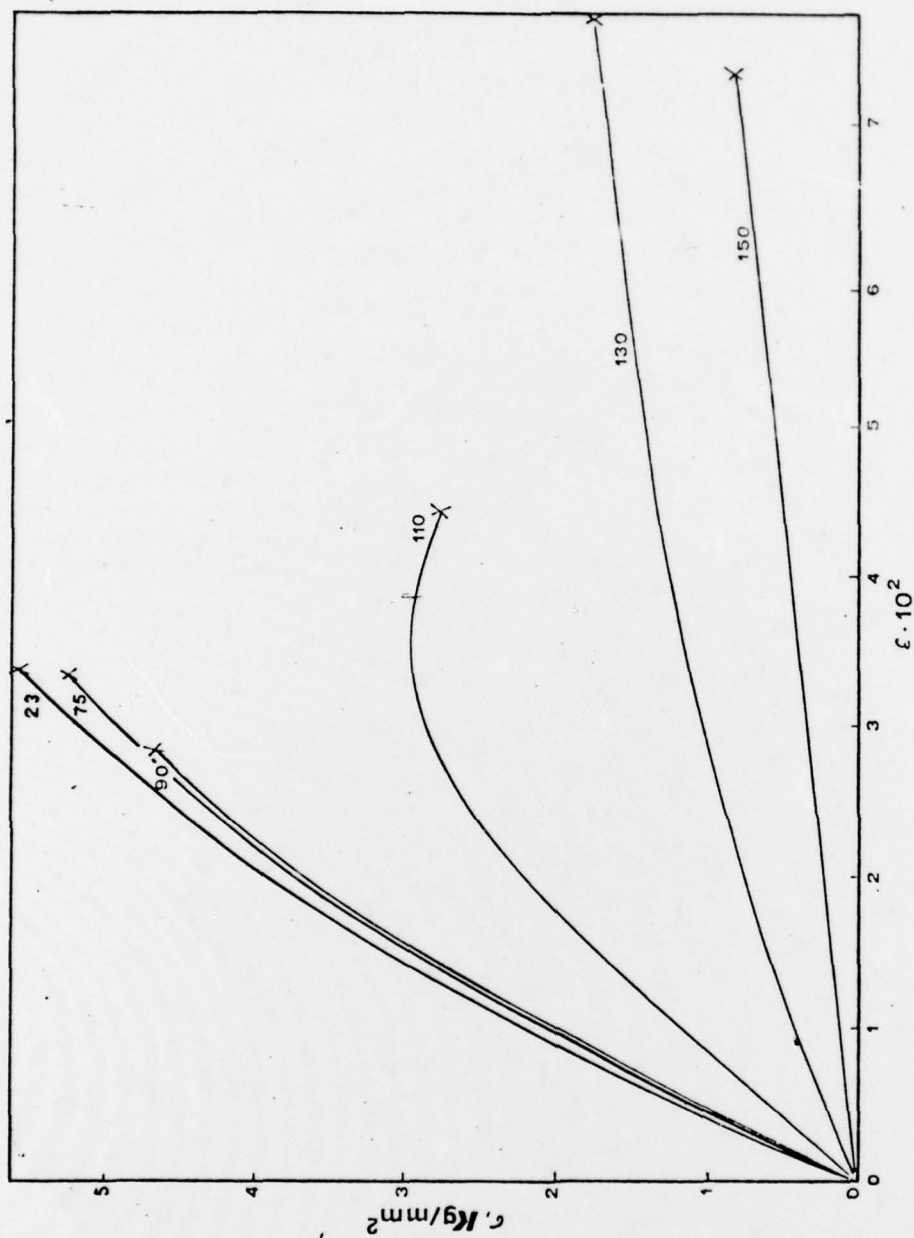


Fig.19) Stress-strain curves for 6-days cured samples at different temperatures.

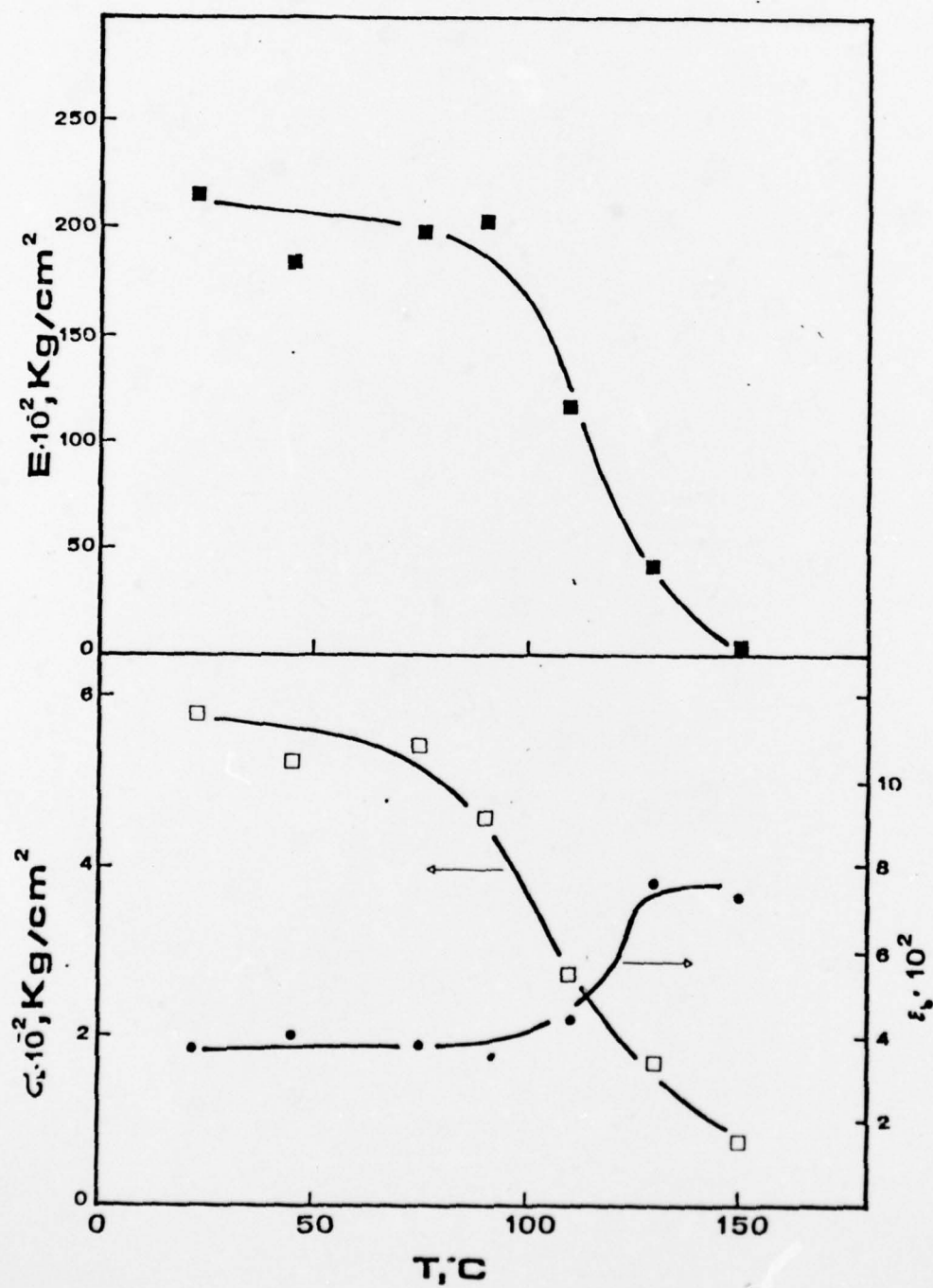


Fig.20) S-9 ultimate properties for 6-days cured samples as function of the temperature

Fig.21) Plasticization effect on S-S curves for samples saturated at 23°C. T=23°C.

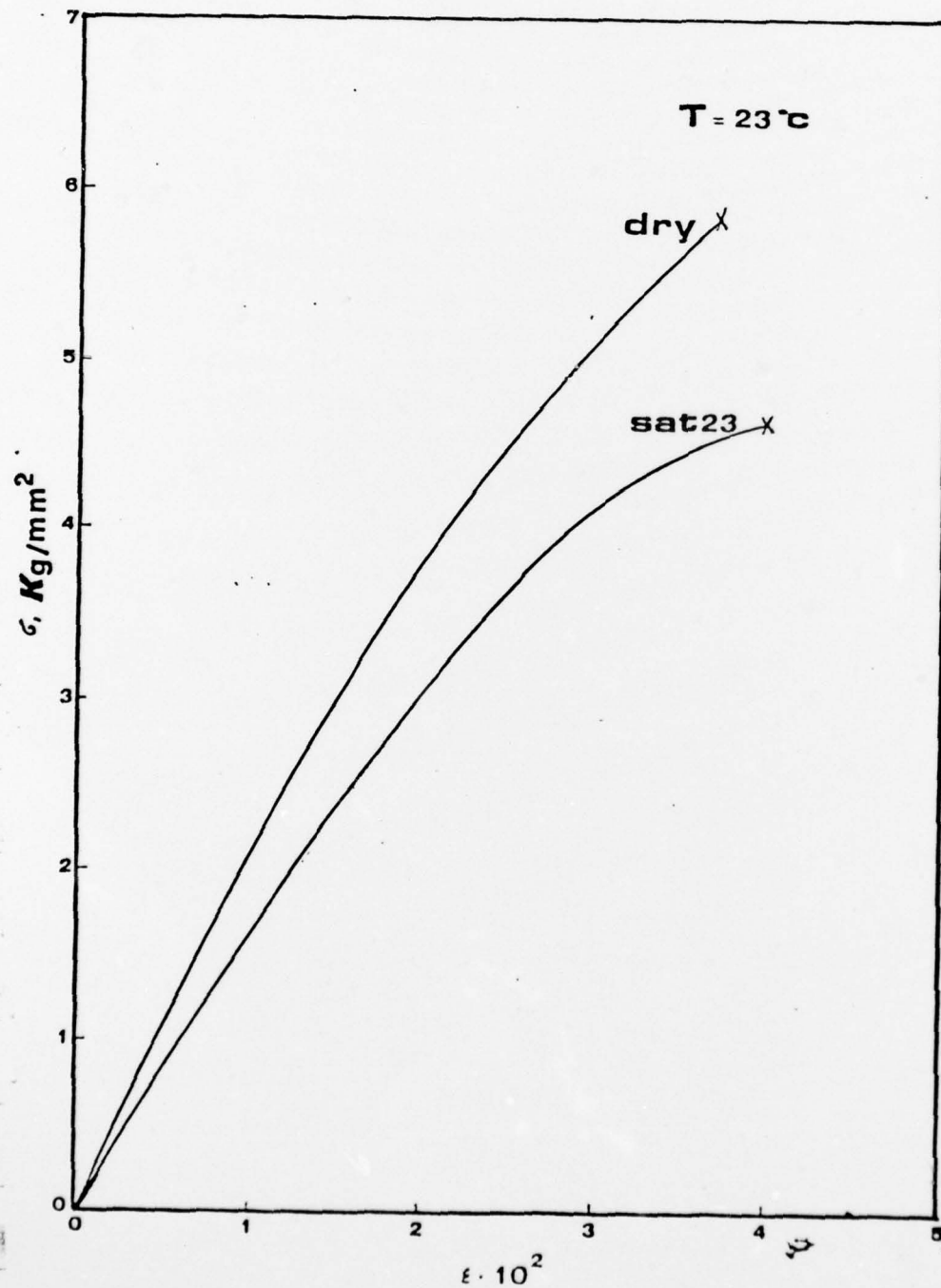


Fig.22) Plasticization effect on S-S curves for samples saturated at 45°C. T=45°C.

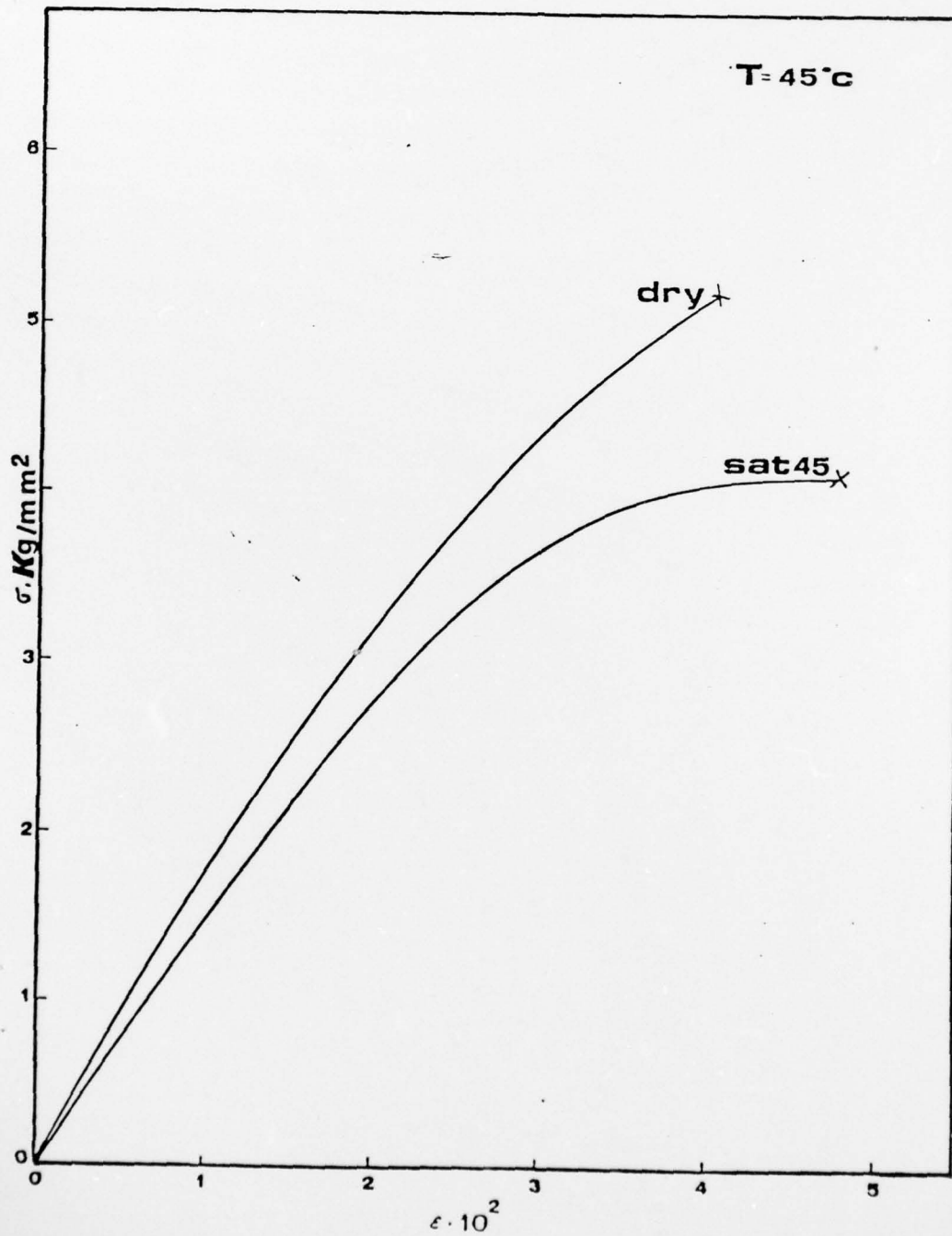


Fig.23) Plasticization effect on S-S curves for samples saturated at 75°C. T=75°C.

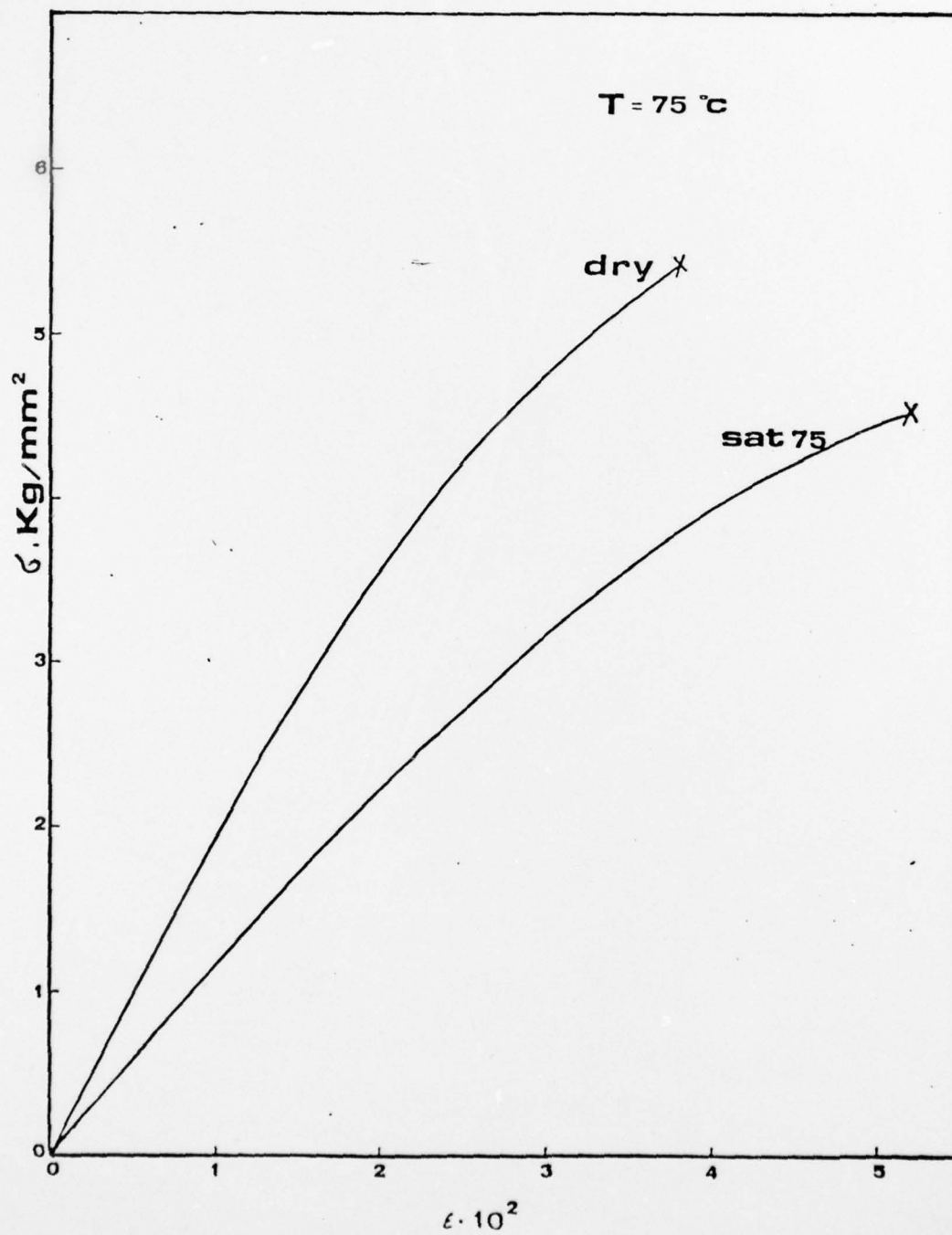
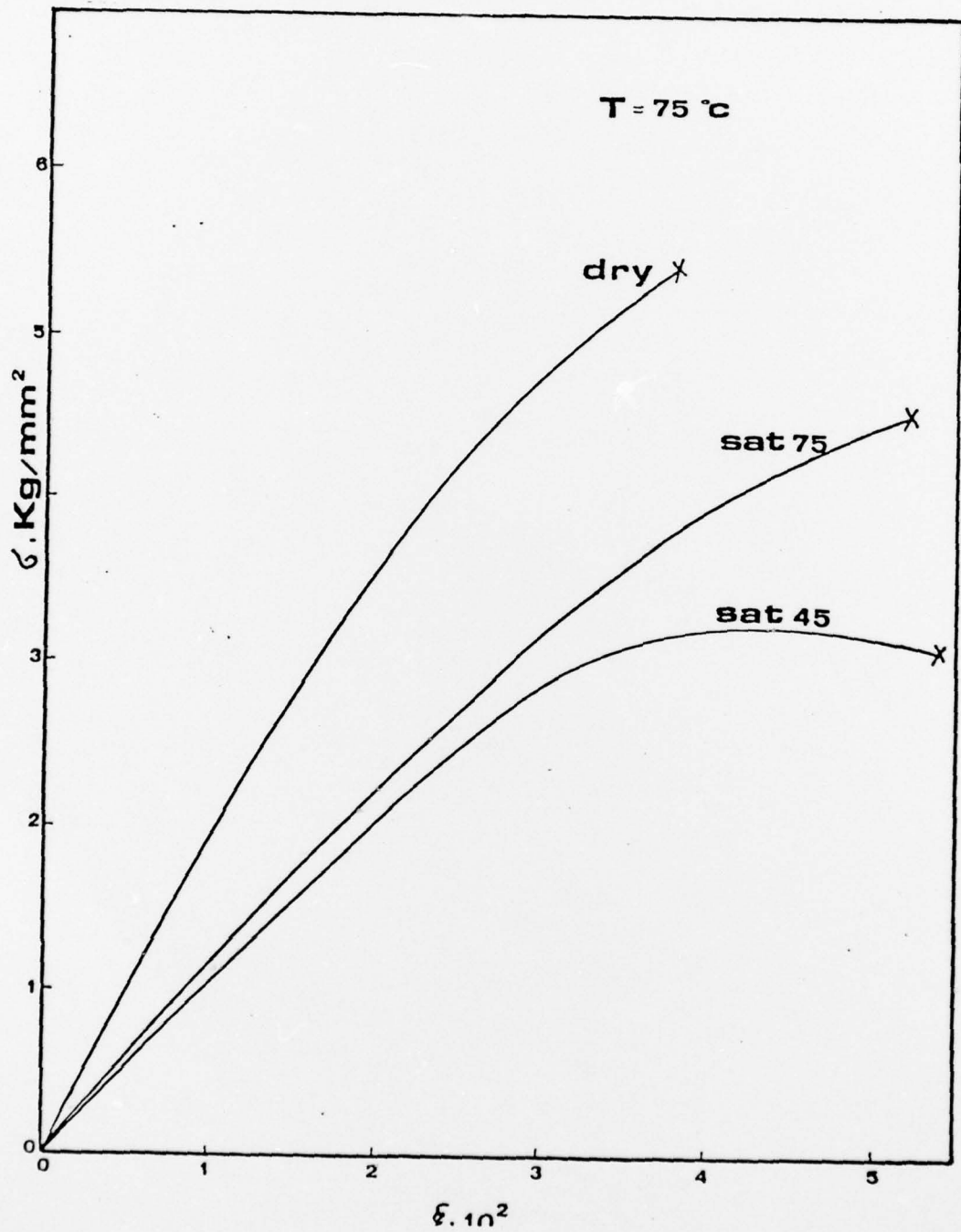


Fig.24) Plasticization effect on S-S curves for samples saturated at 45° and 75°C. Test temperature $T = 75^{\circ}\text{C}$.



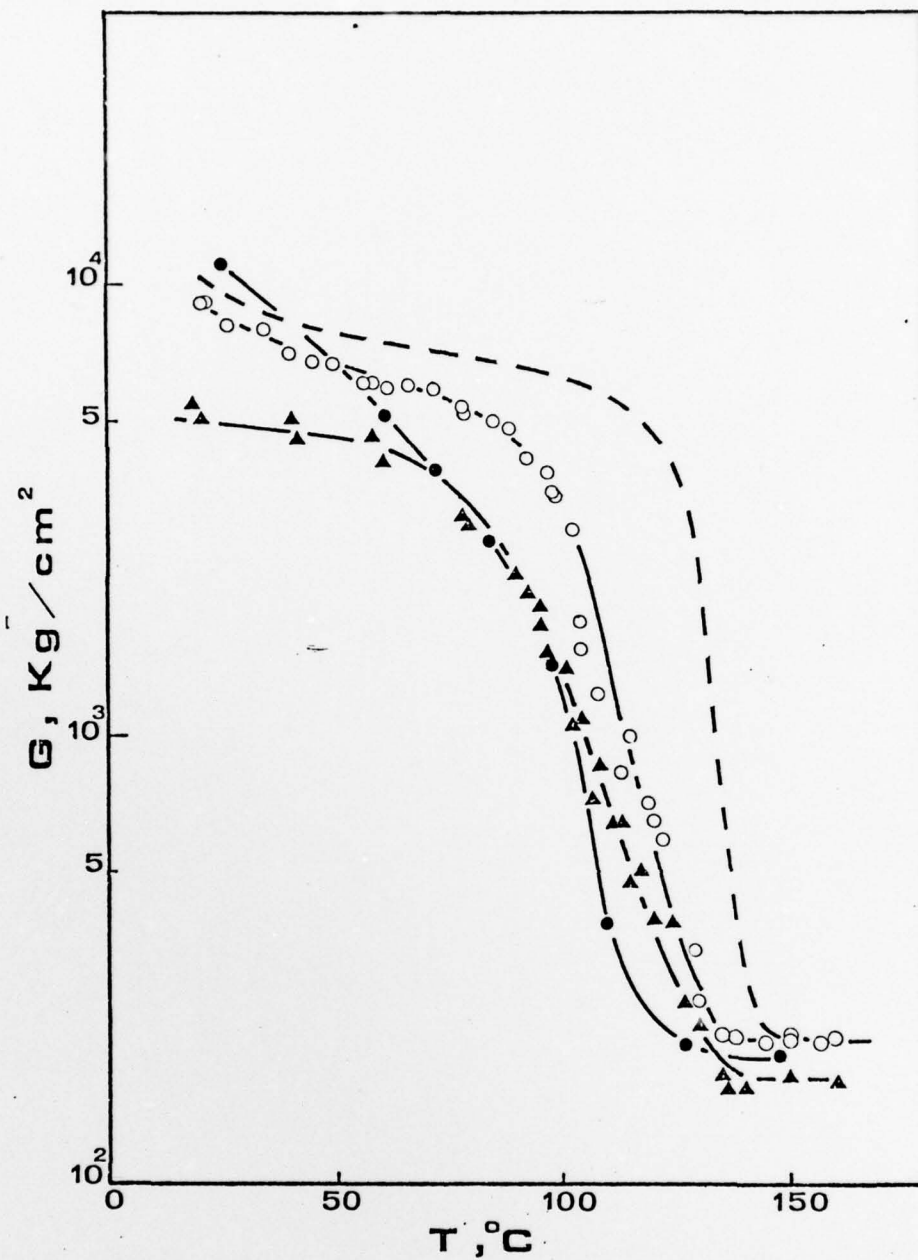


Fig.25) Torsional test results for 3-days cured samples. Dotted line: dry samples.
 Open circles: saturated at 75°C. Triangles: saturated at 45°C.
 Solid circles: saturated at 23°C.

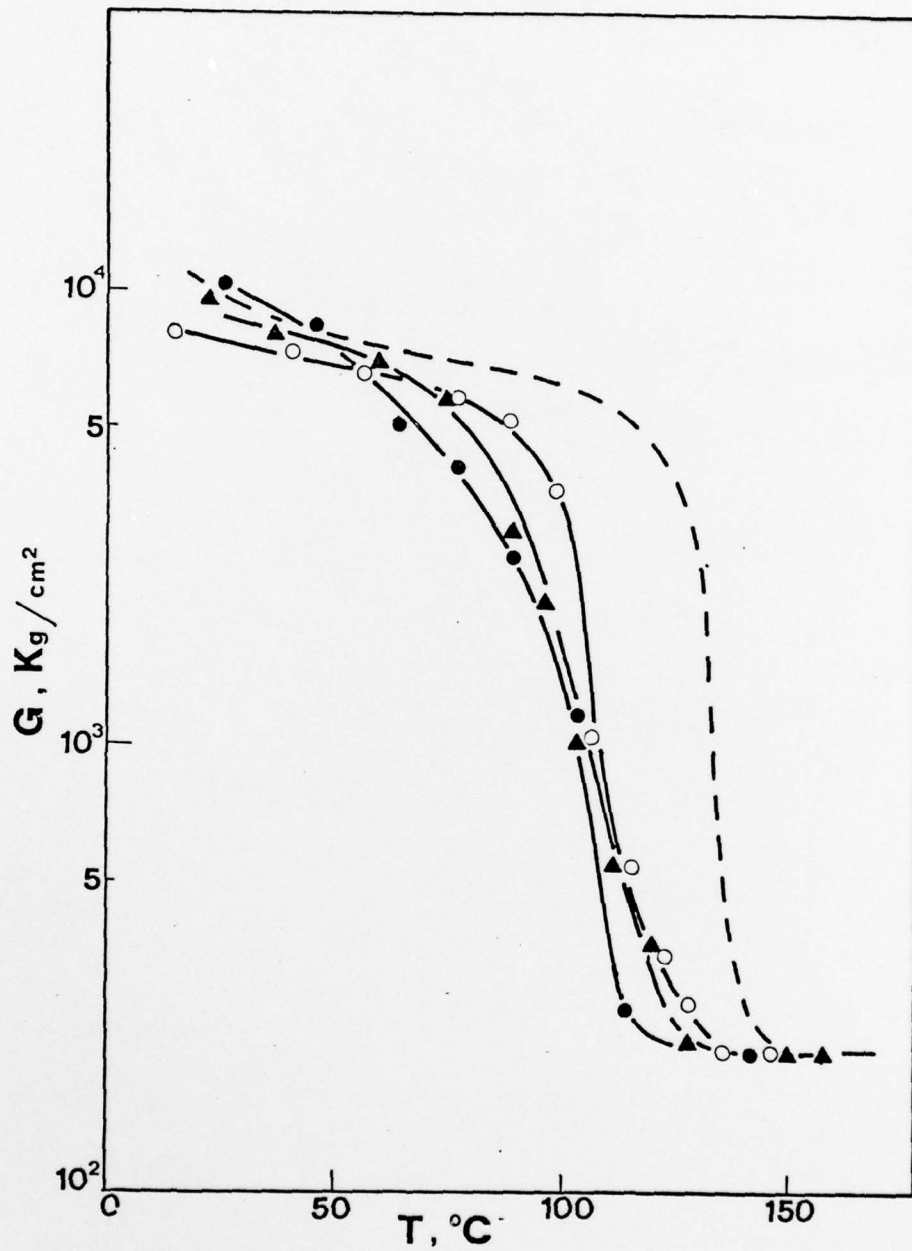


Fig.26) Torsional test results for 6-days cured samples. Dotted line: dry samples.
 Open circles: saturated at 75°C. Triangles: saturated at 45°C.
 Solid circles: saturated at 23°C.

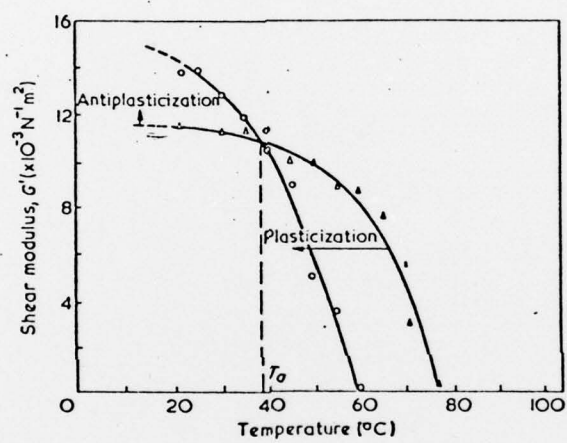


Fig.27) Antiplasticization effects on a Clash-Berg diagram(24).

Antiplasticization-plasticization transition for unplasticized(triangles)
and plasticized(circles) PVC.

